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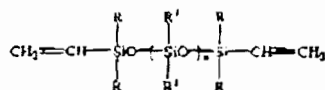
Particulate fillers are known to be useful additives for incorporation into liquid silicone polymer compositions. Such fillers apparently not only can extend and reinforce the cured compositions produced therefrom, but also can favorably influence thixotropic behavior in such compositions. Thixotropic behavior is presently preferred in compositions used in the practice of this invention. A terminal silanol (Si—OH) group makes such silanol siloxanes susceptible to reaction in curing, as is believed desirable.

It is believed that all or a part of component B can be replaced with a so called silanol vinyl terminated polysiloxane while using an organotin compound as a suitable curing catalyst as is disclosed in U.S. Pat. No. 4,162,356. However, it is presently preferred to use vinyl substituted polysiloxanes in component B.

A polymer composition useful in this invention can contain curable silicone resin, curable polyurethane, curable fluorosilicone, curable modified polyurethane silicones, curable modified silicone polyurethanes, curable acrylics, polytetrafluoroethylene, and the like, either alone or in combination with one or more compositions.

One particular type of silicone composition which is believed to be well suited for use in the controlled placement step of the method of the invention is taught in U.S. Pat. Nos. 4,472,470 and 4,500,584 and in U.S. Pat. No. 4,666,765. The contents of these patents are incorporated herein by reference. Such a composition comprises in combination:

- (i) a liquid vinyl chain-terminated polysiloxane having the formula:



wherein R and R' are monovalent hydrocarbon radicals free of aliphatic unsaturation with at least 50 mole percent of the R' groups being methyl, and where n has a value sufficient to provide a viscosity of about 5000 centipoise to about 2,000,000 centipoise at 25° C.,

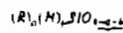
- (ii) a resinous organopolysiloxane copolymer comprising:

- (a) (R²)₂SiO_{0.5} units and SiO₂ units, or
(b) (R³)₂SiO_{0.5} units, (R³)₂SiO units and SiO₂ units, or

- (c) mixtures thereof, where R² and R³ are selected from the group consisting of vinyl radicals and monovalent hydrocarbon radicals free of aliphatic unsaturation, where from about 1.5 to about 10 mole percent of the silicon atoms contain silicon-bonded vinyl groups, where the ratio of monofunctional units to tetrafunctional units is from about 0.5:1 to about 1:1, and the ratio of difunctional units to tetrafunctional units ranges up to about 0.1:1;

- (iii) a platinum or platinum containing catalyst, and

- (iv) a liquid organohydrogenopolysiloxane having the formula:



in an amount sufficient to provide from about 0.5 to about 1.0 silicon-bonded hydrogen atoms per silicon-bonded vinyl group of above component (i) or above subcomponent (iii) of, R⁴ is a monovalent hydrocarbon radical free of aliphatic unsaturation, and has a value of from about 1.0 to about 2.1, b has a value of from

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0.1 to about 1.0, and the sum of a and b is from about 2.0 to about 2.7, there being at least two silicon-bonded hydrogen atoms per molecule.

Optionally, such a composition can contain a finely divided inorganic filler (identified herein for convenience as component (v)).

For example, such a composition can comprise on a parts by weight basis:

- (a) 100 parts of above component (i);
(b) 100-200 parts of above component (ii);
(c) a catalytically effective amount of above component (iii), which, for present illustration purposes, can range from about 0.01 to about 3 parts of component (iii), although larger and smaller amounts can be employed without departing from operability (composition curability) as those skilled in the art will appreciate;
(d) 50-100 parts of above component (iv), although larger and smaller amounts can be employed without departing from operability (curability) as those skilled in the art will appreciate; and
(e) 0-50 parts of above component (v)

Embodiments of such starting composition are believed to be available commercially from various manufacturers under various trademarks and trade names.

As commercially available, such a composition is commonly in the two-package form (which are combined before use). Typically, the component (iv) above is maintained apart from the components (i) and (ii) to prevent possible gelation in storage before use, as those skilled in the art appreciate. For example, one package can comprise components (i) and (ii) which can be formulated together with at least some of component (ii) being dissolved in the component (i), along with component (iii) and some or all of component (v) (if employed), while the second package can comprise component (iv) and optionally a portion of component (v) (if employed). By adjusting the amount of component (i) and filler component (v) (if used) in the second package, the quantity of catalyst component (iii) required to produce a desired curable composition is achieved. Preferably, component (iii) and the component (iv) are not included together in the same package. As is taught, for example, in U.S. Pat. No. 3,436,366 (which is incorporated herein by reference), the distribution of the components between the two packages is preferably such that from about 0.1 to 1 part by weight of the second package is employed per part of the first package. For use, the two packages are merely mixed together in suitable fashion at the point of use. Other suitable silicone polymer compositions are disclosed in the following U.S. patents:

U.S. Pat. No. 4,032,502 provide compositions containing a linear polydiorganosiloxane having two siloxane bonded vinyl groups per molecule, organosiloxane that is soluble in such linear polydiorganosiloxane and comprised of a mixture of a polyorganosiloxane and a polydiorganosiloxane, platinum-containing catalyst, a platinum catalyst inhibitor, and a reinforcing silica filler whose surface has been treated with an organosilicone compound.

U.S. Pat. No. 4,108,825 discloses a composition comprising a triorganosiloxy end-blocked polydiorganosiloxane, an organohydrogensiloxane having an average of at least 2.1 silicon-bonded hydrogen atoms per molecule, a reinforcing silica filler having a surface treated with an organosilicone compound, a platinum catalyst, and ceric hydrate. Such silicone polymer composition is desirable when a web is being prepared which has flame retardant properties.

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U.S. Pat. No. 4,162,243 discloses a silicone composition of 100 parts by weight triorganosiloxy end-blocked polydimethylsiloxane, reinforcing amorphous silica that is surface treated with organosiloxane groups, organohydrogensiloxane, and platinum catalyst.

U.S. Pat. No. 4,250,075 discloses a liquid silicone polymer composition that comprises vinyltriorganosiloxy end-blocked polydiorganosiloxane, polyorganohydrogensiloxane, platinum catalyst, platinum catalyst inhibitor, and carbonaceous particles. Such a silicone polymer composition is useful when a web of this invention is being prepared that has electrically conductive properties.

U.S. Pat. No. 4,427,801 discloses a curable organopolysiloxane of liquid triorganosiloxy end-blocked polydiorganosiloxane wherein the triorganosiloxy groups are vinyl dimethylsiloxy or vinylmethylphenylsiloxy, finely divided amorphous silica particles treated with mixed trimethylsiloxy groups and vinyl-containing siloxy groups, organopolysiloxane resin containing vinyl groups, organohydrogensiloxane, and a platinum containing catalyst.

U.S. Pat. No. 4,500,659 discloses a silicone composition of liquid triorganosiloxy end-blocked polydimethylsiloxy wherein the triorganosiloxy units are dimethylvinylsiloxy or methylphenylvinylsiloxy, a reinforcing filler whose surface has been treated with a liquid hydroxyl end-blocked polyorganosiloxane which is fluorine-substituted, a liquid methylhydrogensiloxane, and a platinum-containing catalyst.

U.S. Pat. No. 4,585,830 discloses an organosiloxane composition of a triorganosiloxy end-blocked polydiorganosiloxane containing at least two vinyl radicals per molecule, an organohydrogensiloxane containing at least two silicone-bonded hydrogen atoms per molecule, a platinum-containing hydrosilation catalyst, optionally a catalyst inhibitor, a finely divided silica filler, and a silica treating agent which is at least partially immiscible with said polydiorganosiloxane.

U.S. Pat. No. 4,753,978 discloses an organosiloxane composition of a first diorganovinylsiloxy terminated polydiorganosiloxane exhibiting a specified viscosity and having no ethylenically unsaturated hydrocarbon radicals bonded to non-terminal silicon atoms, a second diorganovinylsiloxy terminated polydiorganosiloxane that is miscible with the first polydiorganosiloxane and contains a vinyl radical, an organohydrogensiloxane, a platinum hydrosilation catalyst, and a treated reinforcing silica filler.

U.S. Pat. No. 4,785,047 discloses silicone elastomers having a mixture of a liquid polydiorganosiloxane containing at least two vinyl or other ethylenically unsaturated radicals per molecule and a finely divided silica filler treated with a hexaorganodisilazane which mixture is then compounded with additional hexaorganodisilazane.

U.S. Pat. No. 4,329,274 discloses viscous liquid silicone polymer compositions that are believed to be suitable and which are comprised of vinyl containing diorganopolysiloxane (corresponding to component B), siloxane hydride siloxane (corresponding to component A) and an effective amount of a catalyst which is a halogenated tetrameric platinum complex.

U.S. Pat. No. 4,442,060 discloses a mixture of 100 parts by weight of a viscous diorganopolysiloxane oil, 10 to 75 parts by weight of finely divided reinforcing silica,

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1 to 20 parts by weight of a structuring inhibitor, and 0.1 to 4 parts by weight of 2,4-dichlorobenzoyl peroxide controlled cross-linking agent.

Such silicone resin compositions shown in the table below have all been used in the practice of this invention. Such compositions of Table I are believed to involve formulations that are of the type hereinabove characterized.

TABLE I

Illustrative Starting Polymer Compositions

MANUFACTURER	TRADE DESIGNATION	COMPONENTS ⁽¹⁾
Mobay	Silopren® LSR 2530	Vinyl-terminated polydimethylsiloxane with fused silica, methylhydrogen polysiloxane
Mobay	Silopren® LSR 2540/1	
Dow Corning	Siastic® S95 LSR	Polysiloxane
General Electric	SLE 5100	Polysiloxane
General Electric	SLE 5106	Siloxane resin solutions
General Electric	SLE 5300	Polysiloxane
General Electric	SLE 5302	Polysiloxane
Shin-Etsu	KE 1017	
Shin-Etsu	DF 1040-30	
SWS Silicone Corporation	Liquid Rubber BC-10	Silicone fluid with silicone dioxide filler and curing agents
GE SLE 5110		Polysiloxane
GE SLE 5108		Polysiloxane

Table I footnote

(1) Identified components do not represent complete composition of the individual products shown.

When a polymer composition of a silicone polymer and a benzophenone is pressured into a porous web as taught herein, protection of an organic web against ultraviolet radiation is improved, and the degradation effects associated with ultraviolet light exposure are inhibited, as may be expected from prior art teachings concerning the behavior of benzophenones.

Surprisingly and unexpectedly, however, when silicone polymer compositions such as used in this invention contain a benzophenone, the resulting composition is believed to display improved viscosity characteristics, particularly thixotropic characteristics, and also curing acceleration, when such a composition is subjected to high shear forces. A presently preferred benzophenone additive useful in the present invention is 2,4-dihydroxybenzophenone.

The regulation of internal and external rheology, and of viscosity, achieved in a characteristically highly viscous polymer composition of the invention is believed to be an important and desirable feature of the benzophenone and silicone polymer compositions which find use in internally coated web manufacture as taught herein.

In such compositions useful in the present invention, a control of compositional rheology, and particularly of complex viscosity, is accomplishable, if desired, by the selective addition of diluent and additives. These polymer compositions characteristically exhibit performance curves indicating substantially level and constant loss modulus, storage modulus, and complex viscosity over extended temperature ranges. The graphic plots of loss modulus, storage modulus, and complex viscosity versus temperature all are believed to characteristically exhibit a sharp knee that shows the moduli increase in value rapidly at cure temperatures.

Preferably, the curing proceeds to a point where the polymer composition is no longer sticky, or tacky, but preferably curing is not allowed to continue to a point where the resulting polymer composition becomes excessively

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hard, rigid, or brittle. Compositions of this invention are controllably curable into polymeric materials which are preferably not sticky or tacky, and which have desirable elastomeric, flexural, and resiliency characteristics.

The contact angle exhibited by a silicone composition used in this invention varies with the particular web which is to be saturated therewith. However, the contact angle of water is generally lower for the non-treated side than the treated side. A combination of the processed web, the silicone polymer and the fluorochemical generally produces higher water contact angles than webs treated only with fluorochemicals. The performance of a polymer composition may be determined by the nature of a previously applied saturant such as a fluorochemical. Suitable starting compositions include 100% liquid curable silicone rubber compositions, such as SLES600 A/B from General Electric, Mobay LSR 2580A/B, Dow Corning Silastic® 595 LSR and Silastic® 590 which when formulated with substituted benzophenone as taught herein will form a contact angle of much greater than 70 degrees, and typically of 90+ degrees, with typical porous webs (such as fabrics) that have a residue of fluorochemical upon (and within) the web from a prior saturation.

The polymer composition used in the practice of this invention can also carry additives into the three-dimensional structure of the web during the pressured application. Further, it is preferable, that any additives be bound into the cured composition permanently as located in the three-dimensional structure of the web. Particularly in the case of fabrics, this desirably positions the additives mainly on surface portions of the encapsulated yarns and fibers in positions where they typically are beneficially located and maintained, or on the surfaces of the internal layer, or on the surfaces of the web, or some combination thereof.

Control of the pressurized application step can be provided at a number of areas since the shear process is sensitive to the viscosity of the polymer composition both at atmospheric pressure and at superatmospheric pressure. The ambient temperature affecting the polymer as it is applied, and the pressure-induced temperature changes occurring during controlled placement of the polymer also play roles in viscosity and therefore the shear process. Of course, the chemical composition of the polymer composition also plays a role in the shear process and assists in the formation of an internal layer and/or internal encapsulation of the fibers or structural elements of the web.

The amount of polymer utilized and the weight add-on thereof are again variable and dependent upon several things such as the treated web, the desired end use of the web, cost and the like. Web weight add-ons can be as little as about 5 weight percent up to about 200 weight percent of the untreated web. For producing breathable, water-repellent fabric webs of this invention, weight add-ons are preferably in the range of about 10 to about 100 weight percent of the weight of the untreated web.

The fluorochemical saturant composition may also contain a bonding agent. The bonding agent can facilitate the bonding of the water repellent chemical and/or the impregnate to the three-dimensional structure of the web within which it is saturated. Mobay Silopren™ bonding agent type LSR Z 3042 and Norsil 815 primer are representative compositions that can be used to facilitate bonding of the water repellent chemicals and/or impregnant to and within the web. Use of the bonding agents is not essential to the practice of this invention, but may improve bonding of the fluorochemical and/or the polymer composition to fibers.

The fluorochemical particularly, and also the bonding agents when used, are preferably affixed to the three-

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dimensional structure of the web prior to the controlled placement of polymer within the web. Complete affixing is not necessary for the fluorochemical. The fluorochemical will apparently facilitate the pressured application of a polymer composition even if the fluorochemical is not preliminarily fixed within or located within the web being treated. However, fixing, especially by sintering, appears to cause the water repellent chemicals to flow and to become better attached to the three-dimensional structure of the web. In this regard, a lesser amount of fluorochemical will remain in place better, and will better facilitate the subsequent pressured application of the polymer, if the sintering or insolubilizing step is performed prior to such a pressured application.

After fluorochemical saturation followed by controlled polymer placement and curing, a web may have a surface contact angle with the polymer of greater than about 70 degrees, and more typically greater than about 90 degrees. Web pressures can involve transverse force or pressure in the range of tens to thousands of pounds per square inch of web surface.

Similar to the functional qualifications achieved by the use of a fluorochemical in the preferred saturating pretreatment step, the polymer introduced by the pressured application step can be defined by its functional qualifications. For example, the silicone polymer produces a contact angle with a fluorochemical treated web of greater than about 70 degrees. The contact angle of a web with a fluorochemical will be within a range of about 90 degrees to about 180 degrees while the contact angle of a fluorochemically treated web with the silicone polymer will be within a range of about 70 degrees to about 180 degrees.

The contact angle exhibited by the silicone polymer can be, if desired, qualified against the particular web saturated with the particular fluorochemical saturant. The selection of a suitable silicone polymer composition may be determined by the nature of the previously applied fluorochemical saturant. The fluorochemical saturant and silicone polymer compositions are, however, not critical to the practice of this invention since wide respective compositional ranges may be involved. In particular, a substantially undiluted liquid silicon rubber which is available from suppliers, such as OE, Dow Corning, and Mobay-Bayer, will characteristically form a contact angle of much greater than about 70 degrees, and typically greater than about 90 degrees, with typical porous webs (such as fabrics) that have a residue of fluorochemical upon (and within) the web resulting from a prior saturation.

The polymer composition can carry additives into the three-dimensional structure of the web in the pressured application steps of the method of the invention. Further, the polymer composition, when cured, is capable of adhering to structural elements, fibers, yarns, and the like, and any additives dispersed therein. Thus, additives are positioned adjacent to or on surfaces of structural elements, yarns, fibers and the like, in a position where they can be beneficial.

Examples of additives that are dispersible in effective amounts in a viscous polymer composition typically at a concentration of about 0.1 to 20 weight percent (based on total composition weight) include ultraviolet absorbers, flame retardants, aluminum hydroxide, filling agents, blood repellents, flattening agents, optical reflective agents, band aligning agents, biocompatible proteins, hydrolyzed silk, and the like. Hydrolyzed silk is a texturing agent that imparts a substantially silky feel to a fabric treated in accordance with the method of the invention regardless of whether or not such treated web or fabric is itself silk.

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Examples of other polymer dispersible agents include those affecting thermal conductivity, radiation reflectivity, electrical conductivity, and other properties. For example, if a metallic sheen and/or thermal or electrical conductivity or infrared background blending is desired, powdered metals may be dispersed therein.

The pressured application of the polymer is sensitive to the viscosity of the polymer composition. Temperature affects the polymer composition by reducing or altering its viscosity. Shear-induced temperature changes occurring during application or during subsequent shear processing of the polymer can affect viscosity. The chemical composition of the polymer also plays a role in the treating process and effects in the treatment of web structural elements (including fibers) and the regulation of the filling of interstices and open cell voids.

Various machines and procedures can be used for performing the process of the invention. Illustrative machines and processes of use which are suitable for use in the practice of this invention, are now described.

An embodiment of apparatus in accordance with this invention is illustrated in the side elevational view in FIG. 4a. Two blades 200 and 210 in opposed relationship to one another are provided in functional combination with means for providing a precisely adjustable gap therebetween through which a web or fabric 300 is drawn while having a polymer composition 220 applied to either one or both surfaces thereof. An enlarged side view of a typical blade 200 or 210 is shown in FIG. 4b. Dimensions A, B, C, D, and E are typically and exemplarily illustrated as, respectively, about 3-1/2 inches, about 1-1/2 inches, about 2 inches, about 1/2 inch, and about 3/8 inch. The narrow edge is preferably milled to a tolerance of about 1/1000 inch continuously along the edge surface of each blade which is typically and illustratively about 38 inches long. Each of the corners of the narrow edge is preferably and illustratively a hard (not beveled or ground) angular edge. Each blade 200 or 210 is typically and illustratively made from carbon steel or stainless steel. The entry angle of the web 300 with the blade is generally not altered in the apparatus of FIG. 4a. Therefore, for purposes of the apparatus illustrated in FIG. 4a, the blade shown in FIG. 4b has a leading edge 260 and a trailing edge 250.

A reservoir of polymer composition is formed preferably on one upper surface of the web or fabric 300 behind (relative to the direction of web movement) an upper one of the blades 200 and 210 which are mounted on a frame (not shown) so as to extend horizontally. As the fabric 300 is drawn through the slit orifice defined between blades 200 and 210, some polymer becomes entrained on the web or fabric surface and moves through such slit orifice, thereby accomplishing pressurized application of the polymer into the web or fabric 300. The slit orifice gap is chosen preferably and illustratively to be slightly smaller than the relaxed thickness of the starting web or fabric.

Referring to FIG. 4a, a second pressured application station is seen to be positioned downstream (relative to the direction of fabric movement) from the pair of opposed blades 200 and 210. While the blades are shown positioned directly opposed to one another, they may be offset so that the advancing web first contacts one blade and then the other. In such a configuration, the blades may also be adjusted to some angle other than 90° to the web, and blade adjustment facilities (not shown) can be used to accomplish this. At this station, a knife blade 230 is provided which has an edge that presses against the web or fabric 300 to reintroduce the polymer composition into the fabric 300.

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One side of blade 230, adjacent to the edge thereof, is strongly biased against an adjacent cylinder or bar 240, which, in the embodiment shown, does not rotate. If desired, bar 240 can be journaled for rotational movement. As the fabric is moved between the blade 230 and the bar 240, it is preferably uniformly compressed. Preferably, the compression force is in the range of about 10 to about 500 pounds per linear inch, although higher and lower forces can be employed. As the fabric 300 passes over the edge of blade 230, it is drawn away at an angle from the blade edge under longitudinal tension. For example, longitudinal tension in the range of from about 0.5 to 10 pounds per inch can be employed. Such pressured application or controlled placement serves to distribute and reintroduce the polymer composition in the web. Excess polymer composition is removed by blade scraping. Passage of the fabric 300 between the blade 230 and the bar 240 and over the edge of the blade 230 is believed to produce shear forces in the polymer composition 220 (within the fabric 300) that facilitate flow and distribution thereof within the three-dimensional matrix of the fabric 300. Concurrently, blade 230 also scrapes excess polymer composition off the fabric's surface in contact with the edge of blade 230.

Both the steps of fluorochemical saturation and of subsequent polymer composition controlled placement are performable, if desired, in production volumes, and at speeds which can be typical of the so-called high end range of fabric finishing lines. The fluorochemical saturation is conveniently accomplished conventionally by using a pad-bath in which the fabric is run through a dilute treating bath (followed by squeeze rollers to remove excess liquid and overlying). In general, any method of applying the fluorochemical would be acceptable. Typically, the web is treated with a fluorochemical and wound on a roll before it is introduced into apparatus of this invention apparatus although, if desired, the fluorochemical treatment could be in-line.

Another embodiment of a machine suitable for accomplishing controlled placement of polymer within a web in accordance with this invention is shown diagrammatically in FIG. 5. At a treatment or control head, pressurized introduction of the polymer composition into the web is first carried out. At a subsequent stage, controlled pressure reintroduction, distribution, and metering of the polymer composition and recovery of excess polymer transpires using a shear knife or blade which applies transverse force against the treated web laterally across the web. In a subsequent stage, further controlled pressure reintroduction and metering takes place by means of another blade, either flexible or rigid, such as, for example, a so-called flex-knife or Spanish knife. Here, additional recovery of excess liquid polymer is accomplished. In all knife-applying states, the excess polymer removed is collected and preferably passed by a recycling system back to the initial, pressurized introduction stage to achieve process operating economies. Still further successive polymer pressure reintroduction stages may be used if desired. The direction of the arrows in the diagrammatic representation of FIG. 5 shows the general direction of movements in the region of the treatment head, including the general direction of polymer movement in the practice of such process.

The apparatus employed in the present invention functions first to apply and preferably concurrently to shear thin and place a polymer composition into a web under pressure. Such polymer composition is then reintroduced, distributed, and metered in a controlled manner in the web with the aid of transversely applied shearing force and compressive force

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such that the polymer composition becomes distributed in the web so that an internal layer of polymer is formed while the fibers are at least partially enveloped while the interstices or open cells are substantially completely filled with the polymer composition in the region of the internal coating, and/or the fibers within the web are partially or fully encapsulated. During treatment, the web is longitudinally tensioned and the pressurized application and the subsequent shearing and compressive actions are successively accomplished in localized zones preferably extending generally laterally across the web (that is, generally perpendicularly to the direction of such longitudinal web tensioning) using transversely applied force exerted locally against surface portions of the web during each controlled placement and shearing operation. The web is conveniently and preferably, but not necessarily, moved longitudinally relative to such laterally extending web processing zones. In treating short lengths of a fabric, the blades may be moved relative to a stationary length of fabric. The pressurized application, shearing and compressing steps are preferably carried out successively or sequentially. Such zones are themselves preferably at stationary locations while the web is moved, but if desired, the web can be stationary while the zones are moved, or both. The result is that the polymer composition flows into the web and is distributed internally generally uniformly to a predeterminable and controllable extent.

A schematic side elevational view of another embodiment of a suitable machine for use in the practice of the invention is shown in FIG. 6. This machine continuously moves a longitudinally tensioned web 60 successively through a pressure station which incorporates a reverse roll coater having rollers 10 and 11, a shear station which incorporates a shear knife 20, and a finishing station which employs at least one so called flex-knife (or Spanish knife) 30. A typical shear knife is illustratively shown in FIG. 4b. For purposes of the apparatus shown in FIG. 6, the knife shown in FIG. 4b has a leading edge 250 and a trailing edge 260. Optionally, but preferably (for reasons of process operating economics) excess polymer composition that is removed from web surfaces in the shear station and finishing station is returned to the pressure station for reuse using liquid recovery and recycle system 40. In the pressure station, polymer 50 is contained within reservoir 51. Roller 12 rotates in the indicated direction so that its circumferential surface, preferably a textured or gravure surface, picks up liquid 50 from reservoir 51 and deposits it on the circumferential surface of roller 10 across a controlled width gap 13 between rollers 10 and 12. Typically, gap 13 is actually less than the unencumbered thickness of the starting web 60. Roller 10 also preferably has a textured or gravure surface. Roller 10, rotating in the roller arrow indicated direction, which is opposite to the direction of travel of web 60, applies the polymer to one surface of the moving web 60, which is typically a fabric. Roller 11 is urged with a compressive force against the back or opposed surface of web 60 and roller 11 rotates in a direction which is the same as that in which web 60 travels. Roller 11 aids in achieving the desired pressurized application of polymer into web 60 from the surface of roller 10.

Referring to FIG. 6, the polymer is believed to be introduced into the web and into the interstices or open cells of the web 60 by the aid of a back-pulling or shearing action resulting from the distorting and pressuring of web 60 caused by rollers 10 and 11 rotating in the same direction. This direction may be the indicated direction with roller 10 rotating against the linear movement of web 60 indicated by web directional arrow 61, or all rollers 10, 11 and 12 may be

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reversed in respective rotational direction so as to cause each roll to turn in an opposite direction relative to that direction which is illustrated by the respective roller arrows in FIG. 6. Regardless of which side of web 60 is back-pulled or subjected to shearing action by a reverse rotating roller, the web 60 is stretched and distorted to pull open the interstices of the web and to aid in forcing polymer 50 into the web 60. This distorting, and particularly this stretching, is believed to facilitate the full and deep introduction of the polymer into the moving web 60. However, it is to be understood that use of a reverse roll coater or other facilities which distort the web at the polymer application stage is not required. Other suitable polymer applicators well known in the art may be used to deposit the polymer on the surface of the web. Thereafter, the polymer may be shear thinned and placed into the web by use of one or more shear knives 20.

The extent of pressurized application of the polymer 50 into the web 60 which occurs between rotating rollers 10 and 11 is controllable to some extent by such variables as the speed of roller rotation, the pressure exerted by rollers 10 and 11 on web 60, the durometer hardness and surface characteristics of each roll 10 and 11 (particularly of the preferred textured or gravure surface of roll 10). However, the pressurized application may also be carried out with rollers 10 and 11 which have finely milled, smooth circumferential surfaces. The viscosity of polymer 50 and the amount of polymer 50 transferred from roll 12 to roll 10 across gap 13 may also be varied to regulate controlled placement of polymer within the web. Feed roller 12 preferably rotates counter to application roller 10. The polymer 50 can be monitored to assure that its homogeneous composition is maintained. If desired, the polymer composition 50 can be altered to adjust to process needs during a continuous treating operation.

The result of the introduction of the polymer 50 into the web 60 which is accomplished between rollers 10 and 11 using a polymer composition 50, which can have the viscosity or consistency of a conventional bathtub caulk composition, is to produce a web 60, or fabric, whose interstices or open cells are substantially completely filled with polymer in the region of the internal layer, or to produce a web having its structural elements or fibers encapsulated, or to produce a web having a combination of an internal layer and encapsulated fibers. For example, in the case of a fabric, the region of the internal layer can be such that spaces (i.e., interstices or open cells) between the fabric's fibers/filaments, or the fabric's yarn members (as the case may be) are filled with polymer 50. However, the amount of polymer 50 which is thus introduced into web 60 can be much less than a saturation level; for example, if desired, the amount introduced can be insufficient even to coat or substantially completely envelope individual fibers of the web. Actually, the polymer 50 can be relatively non-uniformly distributed in the web after such pressurized application. The action of the shear knife 20 in the next zone of processing is such as to smooth out and to make uniform the distribution of polymer 50 in web 60. Also, the shear knife 20 helps regulate the amount of polymer 50 that is allowed to remain in web 60. While one shear knife is shown, it may be desired use a plurality of such knives in sequence to provide a series of shear thinning stations.

After the shear zone, if desired, a top coat polymer can additionally be introduced; for example, just before or after a flex knife 30. By overcoating for example, the original polymer with a dilute or very thin second or top coat, a more lightly cross linked encapsulated or enveloped product may be achieved, or surface properties of the product can be

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varied or improved. For example, the top coating can comprise a dilute dispersion of a fluorochromic fabric treating composition. In a web treated therewith, such treatment enhances surface properties of the web, such as by increasing grease or chemical penetration resistance, or soil resistance, or the like. The dilute fluorochromic dispersion can be applied by spraying, misting, or the like. Both treating agents then enter a curing stage, which can be accomplished conveniently by passing the treated web through an oven wherein the temperature and web residence time are sufficient to cure both the fluorochromic and polymer compositions to a desired extent, or by radiation, if desired.

The amount of polymer composition actually introduced through the controlled placement, and into the preferably stretched openings of the interstices of the web 60 is influenced by such factors as the velocity of movement of web 60, the viscosity characteristic of polymer 50, the compressive pressure exerted by roll 10 against roll 11, the longitudinal tension exerted upon the tensioned web 60, the force of blade 20 against the web, the angle of blade 20 relative to the web, the number of shear blades used, the polymer distribution achieved by shear blade 20 and by scraper flex knife(s) 30, and the like. In particular, the polymer reintroduction and distribution believed to be achieved by bar or shear knife 20 is achieved by the exertion of a pressure against moving tensioned web 60. The shear force and the temperature elevation due to such shear force results in the polymer 50 flowing into the three-dimensional structure of the web 60.

Preferably, the polymer 50 is thixotropic. The flowing of the polymer 50 into the web 60 using controlled liquid rheology preferably does not result at the time of controlled placement in a fluid viscosity which is so low as to cause the impregnant to spread into and be distributed substantially uncontrolled throughout the web 60. However, the flowing activity of the polymer is preferably accomplished using a polymer 50 which has a controllable rheology and viscosity such that a polymer 50 will achieve a desired internal layer and/or envelopment of individual fibers of the web 60. Particularly when the web 60 is a fabric, this envelopment is preferably a surrounding of the fabric's individual fibers with a localized layer or film of polymer while an internal layer is formed.

A plurality of web tension control devices 10 can be used in the region of metering bar or shear knife 20 and in the region of reintroduction scraper flex knives 30 along web 60 in order to provide the capacity for precision control of the tension exerted on web 60 and of the compressive pressures and shear forces exerted on web 60 at the metering bar or shear knife 20 and flex knives 30.

As shown in FIG. 6, the machine preferably includes an polymer 50 recovery and recycling system which more preferably also includes a filtering subsystem, such system being diagrammatically represented and indicated by line path 40. This system includes a collection tray, or pan, 41, positioned under and behind the moving web 60 to collect along the sides of web 60, the excess impregnating liquid as it is wiped from the web surface contacted by the shear knife 20 and/or by the recovery knives 30 and passed laterally into pan or tray 41. From the recovery collection tray 41, the excess polymer 50 is pumped back through a filter (not shown) into the reservoir 51 of the reverse roll coater for loading and distribution on the surface of roller 12, transfer to roller 10, and reapplication to portions of continuously moving web 60. The ability to reuse the excess polymer 50 wiped from the moving web 60 rather than losing such

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polymer within the process makes the entire process more economically attractive.

Another embodiment of a machine in accordance with this invention is shown schematically in side elevation in FIG. 7. In this embodiment, rollers 10 and 11 of the FIG. 6 methods and apparatus are replaced with a combination of a reservoir 51, and one or more bars or shear knives 100. A typical shear knife is illustratively shown in FIG. 4b. For purposes of the apparatus shown in FIG. 7, the knife shown in FIG. 4b has a leading edge 250 and a trailing edge 260. The reintroduction bar or shear knife 100 shear thins the polymer 50 which is applied or deposited onto the moving web 60 from the reservoir 51 as a liquid or bath. The web 60 in effect constitutes a retaining wall for a part of the reservoir 51. The reservoir 51 thus functions to hold a pool of the polymer composition 50 against a surface of the moving web 60 which in the embodiment shown, is moving vertically upwardly. The bar or shear knife 100 functions to apply pressure or force upon the polymer composition polymer 50 that was deposited on the web 60, thereby to shear thin the polymer 50 and cause it to penetrate the web 60. The knife 100 also serves to distribute and move the polymer in the web and to accomplish envelopment of the fibers thereof. Excess polymer 50 is also scraped away by knife 100. Optionally, one or more of flexible or rigid knives 100 function to further reintroduce and distribute the polymer 50 and to envelope fibers of web 60 while forming an internal polymer layer within the web, or to produce a web having its structural elements or fibers encapsulated, or to produce a web having a combination of an internal layer and encapsulated fibers. The knives 110 can be considered to function in a manner which is equivalent to the knives 30 on the treated surface of web 50 in the FIG. 6 methods and apparatus.

Typically, any polymer scraped from the moving web 60 by bar knife 100 falls directly back into the reservoir 51. Polymer scraped from the moving web 60 by scraper knife 110 is collected in sloping trough 120 and returned by falling along the indicated dotted line path to the reservoir 51. Longitudinal tension control of the moving web 60 is regulated by tension control devices 70 (such as a series of rollers) from a region beginning after reservoir 51 and extending to an oven 80 along the path of web 60 travel.

Relative to the FIG. 7 embodiment, the FIG. 6 embodiment is believed to exhibit a wider degree of control in the practice of the present controlled placement process. Particularly, both the initial applied amount and the successive pressurings of, a polymer 50 are precisely controllable. Relative to the FIG. 6 embodiment, the FIG. 7 embodiment is characterized by the capability for operation at higher web 60 transport speeds, typically at speeds characteristic of higher end commercial fabric finishing line operations. The embodiment shown in FIG. 6 is believed to be suitable for producing internally coated fabrics when the fabrics are of the thicknesses characteristic of garments, and where deeply controlled pressured placement over distances extending perpendicularly into and through a web of fabric greater than about 1/16 inch is not generally required.

FIG. 12a depicts a schematic, side elevational view of another method and apparatus for practicing the present invention. In this method and apparatus, a continuous web 74 is moved along a web pathway from a supply roll 76 to a take-up roll 77.

In a first functional processing station 78, a polymer composition is applied to the upper face 79 of web 74 by a polymer applicator such as a conventional reverse roll coater 81. In the reverse roll coater 81, the polymer composition is

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applied to the surface of a reversely rotating (relative to the direction of travel of web 74) coating roll 82 from a nip region reservoir 83 formed between the coating roll 82 and a transfer roll 84 (which rotates in the direction of travel of web 74, but whose surface does not contact web 74). The web 74 is transversely compressed between coating roll 82 and drive roll 86 as it passes through station 78. Thus, the polymer composition is applied under a positive pressure against face 79 by coating roll 82 which functions to cause the composition to be forced into web 74. A present preference is to use a coating roll 82 which has smooth, chrome plated surfaces. It is also possible to apply the polymer composition to the upper face 79 of the web 74 without any force, leaving the controlled placement and shear thinning for a subsequent step or series of steps, such as by the force of the shear knives as described below.

Largely for purposes of controlling the alignment of web 74 with rolls 82 and 86, the web 74 is tensioned by coating clutching rolls 87, 88 and 89. After the web 74 passes over guide roller 91 on the web pathway from supply roll 76, the web 74 passes over roll 87, between rolls 87 and 88, around roll 88, and between rolls 89. The clutching rolls 87, 88 and 89 are components of a conventional web clutching mechanism (not detailed) which provides for adjustments between rolls 87, 88 and 89 so that selective tensioning of web 74 is achieved along the web pathway between the clutching rolls 87, 88 and 89 and the nip region 92 defined between rolls 82 and 86 with the intervening roller roll 93 being used for guidance of web 74. The clutching rollers 87, 88 and 89 also function to smooth out and extend web 74 before it enters the coater methods and apparatus 81 so that in the methods and apparatus 81, the web will have polymer composition uniformly applied thereto.

After passing nip region 92 the web 74 is controllably longitudinally tensioned along the web pathway extending from nip region 92 to compensating and regulating coating tension rollers 94, 95 and 96. The tension rollers 94, 95 and 96 are components of a conventional web tension adjusting and regulating mechanism (not detailed) which provides for on-line, in-stream operator controlled adjustments between rollers 94, 95 and 96 that permit selective control of the tautness of web 74 particularly in the web pathway region from nip region 92 to rollers 94, 95 and 96. In the event a reverse roll coater is not utilized, the tension will be controlled in the region between rolls 87, 88 and 89 on one hand, and rolls 94, 95 and 96 on the other hand.

Along the tensioned web pathway region, the web 74 successively passes through each one or more of a series of processing stations 98, 99 and 100. While three processing stations are shown, more or less could be utilized in accordance with this invention. At each of the stations 98 and 99, a substantially non-flexible shear knife 101 and 102, respectively, extends laterally across web 74 with the web 74 being entirely unsupported on the lower face thereof which is opposed to upper face 79 and to the respective blades of each shear knife 101 and 102. A typical shear knife is illustratively shown in FIG. 4b. For purposes of the apparatus shown in FIGS. 12a, 12b, and 12c, the knife shown in FIG. 4b has a leading edge 250 and a trailing edge 260. Both to control the amount and type of shear force independently applied by each knife 101 and 102 the web 74 passes over each knife edge in a contacting relationship and three blade rolls 105, 106 and 107, that are provided in a typically fixed (but off-line adjustable) relationship relative to knives 101 and 102. The blades 101 and 102 are adjustable both vertically and angularly. By adjusting the vertical height of

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each blade relative to the web path, the force of each blade against the web can be controlled. By adjusting the vertical height of the blade rolls, the shear force can be controlled and the angle at which the web contacts the blades can also be controlled.

Relative to the direction of web 74 travel, blade rolls 105 and 106 thus are positioned so that roll 105 is on the lead side, and roll 106 on the trailing side, of knife 101 while blade rolls 106 and 107 are positioned so that roll 106 is on the lead side, and roll 107 is on the trailing side of knife 102. The angle of inclination or tilt of each blade 101 and 102 relative to the vertical is adjustable over a wide range, but it is presently preferred to adjust the blade inclination angle for each blade between about $\pm 45^\circ$ relative to the vertical with the web 74 being horizontal. In the embodiment shown, each respective blade is functionally associated with a knife back support or holder 108 and 109, respectively. Each support 108 and 109 permits its associated blade 101 and 102 to be vertically and angularly positioned relative to a supporting frame (not shown).

Another adjustable variable is the amount of angular web depression which, in the embodiment shown, extends downwardly, achieved by the web in its passage over the circumferential edges of adjacent rolls 105 and 106 relative to knife 101, and in its passage over the circumferential edges of rolls 106 and 107 relative to knife 102. Considering the place where the knife 101 or knife 102 contacts the web to be a hypothetical point, the angle of the knife 101 or knife 102 relative to the web can be in the range of about 30° to about 140° .

While it is presently preferred to employ shear knives 101 and 102 which have straight edges to shear thin the polymer composition, it will be appreciated that shear knives having somewhat curved edges can be used, if desired. For example, when treating a web which displays differential longitudinal stretch characteristics laterally thereacross in response to a uniform laterally applied warp tension, it appears to be possible to equalize the shear forces applied to a web by employing a suitably curved shear knife which appears to compensate for such a differential stretch characteristic.

While it is presently preferred to employ shear knives 101 and 102 which have sharp edges, shear knives can also be used which have dull or rounded edges. It is also preferred to use knives having edges which are surface finished to a uniformity of at least about root mean squared (RMS)8.

While it is presently preferred to employ shear knives 101 and 102 which are formed of steel, other materials of knife construction could be used if desired, such as metal alloys, non-metallic composites, and the like. The shear knives are preferably hardened or otherwise treated to reduce wear.

Those skilled in the art will appreciate that the amount of shear force applied by one or more shear knives 101 or 102 transversely against a web 74 is a function of many variables with probably the most important or principal variables being the polymer viscosity, the longitudinal web tension, and the positioning of the shear knives 101 and 102 relative to the web 74 during operation.

When a suitable and preferred level of applied shear force and web tensioning have been achieved to produce a product having encapsulated or enveloped fibers and/or an internal coating, or both, one can usually hear a distinctive sound in the region of a shear blade 101 and 102. This sound can also be heard in the vicinity of shear blades being used in the operation of other processes described herein. This sound can in fact be used by an operator as a rough guide as to whether or not the operator is succeeding in producing a

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product with controlled polymer placement containing enveloped fibers and/or an internal coating, or both.

Blade roll 105 also functions as a compensator roll for mechanically adjusting and controlling web tension before shear thinning begins. Also, conveniently and preferably the web tension is sensed electronically, and then roll 105 is automatically raised or lowered to achieve web tensioning adjustments so as to maintain a preset predetermined tension in web 74.

After passing over roll 107, the web 74 is passed over the circumferential surface of a conventional padder roll 111. Between the blade roll 107 and the padder roll 111, a flexible so-called "flex-knife" or "Spanish knife" 100 is positioned. Preferably, the blade of this flexible knife 100 is inclined at an angle with respect to the web 74 passing thereagainst so that the knife 100 exerts a compressive force against the face 79 of web 74 with opposed face 103 being entirely unsupported. The angle with respect to a (hypothetical) perpendicular line extending into a (hypothetical) straight line extending from the circumferential edge of roll 107 to the circumferential edge of roll 111 can range from about 30° to about 140° for the adjustment of the inclination angle of the flex knife. To provide adjustability for flexible knife 100, knife 100 is functionally associated with a mounting bracket or back support 113 which in turn is adjustable relative to methods and apparatus frame (not shown).

In the embodiment shown in FIG. 12a, the padder roll 111 is not employed as a web 74 treating means. It is not necessary to use the padder roll 111 in all applications. It is typically only used when tension is needed through the nip of the padder roll.

After leaving the mechanical tension compensator rolls 94, 95 and 96, web 74 is under reduced or preferably minimal tension and is led along a pathway which extends over spacer rolls 113 and 114. Alternatively, the web 74 may pass directly from the tension rolls 94, 95 and 96 into the curing oven 119. In the region over spacer rolls 113 and 114, and generally between tension roll 96 and idler roll 117, a platform 116 is conveniently positioned which can incorporate suitable instrumentation panels, operating controls and the like so that an operator can observe the operation of the apparatus in accordance with this invention and then control and regulate the same. A position which is suitable for operator observation of a web in progress that is located in the vicinity of a tenter frame 118 is desirable because it has been observed that a web being processed can experience some distortion owing to the forces exerted thereon. These distortions can be metered and observed and then the tenter frame 118 adjusted by the operator so that, as the web passes therethrough, the web can be straightened or shaped either longitudinally or laterally, as desirable or considered necessary for an individual web. If desired, the tenter frame 118 can be automatically operated to apply tensioning forces to a web in accordance with a predetermined program, or the like. It is to be understood, however, that a tenter frame may not always be necessary or desirable. Many webs may be processed in accordance with the principles of this invention without use of a tenter frame or other transverse tensioning device. In such cases, the web will pass directly into the curing ovens from the tension rolls 94, 95 and 96 or from the spacer rolls 113 and 114.

The tenter frame 118 also provides the start of a new zone of limited longitudinal and transverse tensioning which extends forwardly along the web pathway from tenter frame 118 through oven 119 to a tension compensator, here shown as utilizing three tension rolls 121, 122 and 123 which are part of a conventional mechanical tension compensator

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subassembly which is similar in structure and function to the compensator subassembly incorporating the previously described tension rolls 94, 95 and 96. The tensioning longitudinally of web 74 as it passes through oven 119 is employed to control the web 74 as it passes through oven 119 as regards web dimensional limits. This tensioning is chosen to be at a level which does not introduce significant distortion into the web, yet web sagging is avoided, as from thermal expansion and elongation. Rollers (not shown) can be used in the oven 119 to avoid sagging and to maintain uniform heat exposure. It has been found for many applications that it is desirable to cure the treated web under substantially no tension. It is preferable that the web be cured in a relaxed state so that its original construction or the physics of its construction can be retained. This is instrumental for maintaining the correct band and minimizing shrinkage.

In addition to serving as tension regulating means, the rolls 121, 122 and 123 also serve to provide a cooling pathway for the web 74 as it emerges from the oven 119 before it passes over guide roller 124 and onto take-up roll 77.

The oven 119 functions to cure the polymer composition selectively placed within the web 74. Oven 119 can be operated with gas or other energy source. Furthermore, the oven could utilize radiant heat, induction heat, convection, microwave energy or other suitable means for effecting a cure which are known in the art. Oven 119 can extend for from about 12 to about 20 yards.

Curing temperatures of from about 320° to about 500° F., applied for times of from about 2 minutes to about 30 seconds (depending upon the temperature and the polymer composition) are desirable. If a curing accelerator is present in the polymer, curing temperatures can be dropped down to temperatures of about 265° F. or even lower (with times remaining in the range indicated).

In place of an oven, or in combination with an oven, a source of radiation can be employed (electron beams, ultra-violet light, or the like) to accomplish curing, if desired.

Less than the full heating capacity of the oven 119 can be used, if desired. For example, only top heating or only bottom heating with respect to the web can sometimes be used as compared to a combination of both top and bottom heating.

The take-up roll 77 is operating at approximately the same speed as the supply roll 76. When the rotational speeds of take-up roll 77 are not synchronized with rotational speeds of the supply roll 76, the tension roll combination of rolls 121, 122 and 123 can be used to take up or reduce web slack, as the case may be.

Web transport speeds can vary widely; for example, from about 2 yards per minute to about 90 yards per minute. Present speeds are from about 35 yards per minute to about 50 yards per minute.

The apparatus and processes described above can be used in various forms or embodiments. Referring to FIGS. 12b and 12c, two alternate variations or modes are seen. In such views, similar components are similarly numbered but with the addition of single prime marks thereto in the case of FIG. 12b and double prime marks thereto in the case of FIG. 12c.

In FIG. 12b, a further stage of web pressurization is introduced after the flex knife 112' and before the tenter frame 118'. Here, the web 74 after passage through the flex knife 112' is passed through the nip region 126 existing between padder roll 111' and associated transfer roll 127 where the web 74' is subjected to compression between such rolls 127 and 111' for the purpose of achieving a better distribution of polymer composition on web 74.

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After leaving nip region 126, the web 74 is retained under some compression against roll 127 by means of retaining bar or roll 128 for similar purposes. As discussed with reference to FIG. 12a, the web 74 may pass directly into the oven 119 without utilizing the tenter frame 118. It is desirable that the web curing start promptly after tension is released in the nip region 126, thus it is preferred that the nip region 126 be located in close proximity to the entrance to oven 119.

If desired, the roll 128 can be replaced by a flex knife (not shown) over whose edge the web 74 passes after departure from roll 127. The flex knife can accomplish substantial further polymer distribution in web 74.

Referring to FIG. 12c, there is seen an embodiment where the web 74 is passed through the nip region of rolls 111" and 127". Here not only is use of the mechanical tension roll combination having rolls 94, 95 and 96 (as in FIG. 12a) eliminated, but also the rolls 111" and 127" serve to end the region of high longitudinal tension in the stages of blade or knife application to web 74 and to provide the desired reduced tension for web passage through a curing station, here illustrated by oven 119" which may or may not use the intervening tenter 118".

FIG. 14 depicts a schematic, side elevational view of a preferred embodiment or methods and apparatus for practicing the present invention. In this embodiment a continuous web 302 is moved under tension along a web pathway from a supply roll 301 to a take-up roll 327.

The primary tension is a result of the differential rate between the driven entrance pull stand designated as 306 and the driven exit pull stand designated as 322, whereby the exit pull stand 322 is driven at a rate faster than the entrance pull stand 306. Other controllable factors which effect tension are the diameters of blade rolls 309, 314, 316, 318, the vertical depth of blades 311, 315, 317; the durometer of the entrance pull stand rolls 304, 305 and rubber roll 321 of the exit pull stand, and the friction as the web passes under the blades.

Web 302 passes between the nip of the two rolls 304 and 305 of the entry pull stand 306. The entry nip is adjustable to produce a force of from about 100 lbs. to about 5 tons on the web, passing between the two rolls. The weight of top roll 305 provides an even distribution of force throughout the web width. Web 302 is flattened at this point and the interstitial spaces are reduced laterally and longitudinally. Bottom roll 304 has micro-positioning capability to provide for gap adjustment and alignment. The top roll 305 composition is chosen based on the durometer of a urethane or rubber roll.

Web 302 continues to move along past idler roll 308 and blade roll 309 and forms an entry angle α and an exit angle β with blade 311. Blade 311 is illustratively shown in FIG. 4b. For purposes of the apparatus of FIG. 14, the blade in FIG. 4b has a leading edge 250 and a trailing edge 260. Entry angle α can be varied by adjusting: (a) the height and diameter of blade rolls 309 and 314, (b) the horizontal position of blade rolls 309 and 314, (c) the angle of blade 311, and (d) the height of blade 311. Similarly, the entry and exit angles of blades 315 and 317, can be varied by adjusting the same devices surrounding each blade.

For illustrative purposes, increasing the height and diameter of blade roll 309 decreases entry angle α . Rotating blade 311 clockwise, with web 302 running left to right, increases entry angle α . Likewise, rotating blade 311 counter-clockwise, with web 302 running left to right, decreases entry angle α . Decreasing the distance between blade roll 309 and blade 311 decreases entry angle α . Increasing the downward depth of blade 311 into web 302 decreases entry angle α .

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The angle of blades 311, 315, and 317 are completely changeable and fully rotational to 360°. The fully rotational axis provides an opportunity for more than one blade per rotational axis. Therefore, a second blade having a different thickness, bevel, shape, resonance, texture, or material can be mounted. Ideally the apparatus contains two or three blades per blade mount. The blade mounts are not shown.

The force or pressure of blade 311 applied against web 302 is determined by the vertical positioning of blade 311 in the blade mount. The greater the downward depth of blade 311, the greater the force or pressure. Blade pressure against the web is also accomplished through the tension of the web as described above.

The same line components that affect entry angle α , also affect exit angle β . Any changes in the height, diameter, or horizontal positioning of blade rolls 309 and 314, affects exit angle β . If the angle of blade 311 is rotated clockwise as described above, entry angle α increases, thus decreasing exit angle β .

As web 302 moves from left to right in FIG. 14, polymer is deposited on web 302 with polymer applicator or dispersion means 310. Polymer applicator 310 can be a pump, a hose, or any available application device for applying polymer onto the surface of the web. Polymer applicator 310 is located directly in front of blade 311. The polymer is immediately shear thinned, placed into, and extracted from web 302 by the leading edge of blade 311, thus controlling the amount of polymer remaining in web 302. The bevel of blade 311 can effect entry angle α and the sharpness of the leading edge of blade 311. A sharper leading edge has a greater ability to push the weave or structural elements of web 302 longitudinally and transversely, increasing the size of the interstitial spaces. As the web passes the leading edge of blade 311, the interstitial spaces snap back or contract to their original size.

As web 302 moves from left to right in FIG. 14, the process of shear thinning and placing polymer into and extracting it out of web 302 is repeated at subsequent blades 315 and 317, thus controllably placing the polymer throughout web 302. Web 302 then passes over idler roll 319 and between driven exit pull stand 322 which consists of rolls 320 and 321. Pull roll 320 is a driven roll proportionally driven at a predetermined rate slower than entry roll 304. Pull roll 321 does not apply pressure so much as it achieves a high degree of surface area in which web 302 must come into contact with. The larger the surface area, the higher the degree of contact friction. Pull roll 321 can be adjusted to have sufficient downward force to eliminate any slippage between web 302 and pull roll 320.

After web 302 passes from exit stand 322, it then moves into an oven 323 for curing. Rolls 324, 325, and 326 provide a tension regulating means and also serve to provide a cooling pathway for web 302 as it emerges from oven 323 before passing onto take-up roll 327.

The cure temperature of oven 323 is thermostatically controlled to a predetermined temperature for web 302 and the polymers used. Machine runs of new webs are first tested with hand pulls to determine adhesion, cure temperature, potentials of performance values, drapability, acoustics, etc. The effect on web 302 depends on the temperature of oven 323, dwell time and curing rate of the polymer. Web 302 may expand slightly from the heat.

Oven 323 functions to cure the polymer composition that is controllably placed into web 302. Oven 323 can be operated with gas or other energy sources. Furthermore, oven 323 could utilize radiant heat, induction heat, convection, microwave energy or other suitable means for

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effecting a cure. Oven 323 can extend from about 12 to 20 yards, with 15 yards long being convenient.

Curing temperatures from about 320° F. to about 500° F., applied for times of from about two minutes to about thirty seconds (depending on the temperature and the polymer composition) are desirable. If a curing accelerator is present in the polymer, curing temperatures can be dropped down to temperatures of about 265° F. or even lower (with times remaining in the range indicated).

The cure temperature of oven 323 and the source and type of cure energy, are controlled for a number of reasons. The cure temperature of oven 323 is controlled to achieve the desired crosslinked state; either partial or full. The source and type of energy can also affect the placement of the polymer and additives. In place of an oven, or in combination with an oven, a source of radiation can be employed (electron beams, ultraviolet light, or the like) to accomplish curing, if desired. For example, by using a high degree of specific infrared and some convection heat energy for cure, some additives can be staged to migrate and/or bloom to the polymer surfaces.

Oven cure dwell time is the duration of time the web is in oven 323. Oven cure dwell time is determined by the speed of the oven's conveyor and physical length of the oven. If the dwell time and temperature for a particular web is at maximum, then the oven conveyor speed would dictate the speed of the entire process line or the length of the oven would have to be extended in order to increase the dwell time to assure proper final curing of the web.

Take-up roll 327 is operated at approximately the same speed as supply roll 301. When the rotational speeds of take-up roll 327 are not synchronized with rotational speeds of supply roll 301, the tension roll combination of rolls 324, 325, and 326 can be used to reduce web slack.

Web speed is proportional to the variable speed of the motor which drives entrance pull stand 306 and exit pull stand 322. Web speed can effect the physics of the polymers as web 302 passes under blades 311, 313, and 317. Web transport speeds can vary widely; for example, from about two yards per minute to about ninety yards per minute.

Typically, and preferably, webs of this invention are characterized by having fiber envelopment layers which range from about 0.01 to about 50 microns.

A presently preferred web which is both fluorochemical and silicone polymer treated and which is breathable, water resistant and rewashable is characterized as being a longitudinally tensionable porous flexible fibrous web having opposed substantially parallel surfaces that are comprised of associated fibers with intersices between the fibers, or is a matrix having cells or pores therein. The web is substantially uniformly impregnated with a fluorochemical and thereafter treated with a silicone polymer composition, to form a web having an internal layer within the web wherein the outer surfaces of the web are substantially free of silicone polymer and the web is breathable and water resistant or waterproof. At least a portion of the fibers or cell walls are encapsulated or enveloped. At least one surface of the web is characterized by having a visual appearance which is substantially the same as the visual appearance of one surface of the starting porous web.

When the web has fibers comprised of a synthetic polymer, the polymer is preferably selected from the group consisting of polyamides, polyesters, polyolefins, regenerated cellulose, cellulose acetate, and mixtures thereof. Preferred webs of this invention are more specifically characterized by having a water drop contact angle in the range of about 90° to about 160°; a rewash capability of at least about

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3; a breathability of at least about 35% of untreated substrate web; and a water repellency rating of at least about 80 prior to washing.

A general process for making a porous web of this invention comprises the steps of: tensioning a flexible, porous web as above characterized, applying a curable shear thinnable polymer composition to at least one web surface and then moving over and against one surface of the tensioned web a uniformly applied localized shear force to: shear thin the polymer composition, uniformly place the composition within the web, at least partially individually encapsulate or envelop surface portions of at least some of said fibers through the web matrix or position said composition in a desired web internal region or some combination of both. Thereafter, the web is subjected to conditions sufficient to cure the composition in said web. Curing is accomplished by heat, by radiation, or both.

A presently preferred process for making a fluorochemical and silicone resin treated web having breathability, water resistance and rewashability which is adapted for continuous operation comprises the successive steps of: impregnating the web with a fluorochemical, longitudinally tensioning the fluorochemical impregnated web while sequentially first applying to one surface thereof a curable silicone polymer composition and concurrently applying a transversely exerted localized compressive force against said surface, and moving over said surface of the web substantially rigid shearing means which exerts transversely an applied, localized shear force against said surface to shear thin the polymer and wipe away exposed portions of silicone polymer composition on said surface, thereby forming an internal layer of silicone polymer and/or enveloping at least some of the fibers or passageways through the matrix, or both; and curing the silicone polymer composition in the web.

The fluorochemical controlled placement operation is conveniently and preferably carried out by the steps of: substantially completely saturating the web with a solution or dispersion of a fluorochemical composition in a carrier liquid; compressing the saturated web to remove therefrom excess portions of said dispersion; and heating said web to evaporate the carrier liquid therefrom. However, any convenient process can be used for accomplishing fluorochemical pretreatment of a web to be used in this invention.

The following text concerns the theory of the invention as it is now understood; however, there is no intent herein to be bound by such theory.

The presently preferred polymer composition used in the treatment of webs by this invention is a non-Newtonian liquid exhibiting thixotropic, pseudoplastic behavior. Such a liquid is temporarily lowered in viscosity by high pressure shear forces.

One aspect of the invention is a recognition that when high forces or sufficient energy are applied to curable polymer compositions, the viscosities of these materials can be greatly reduced. Conversely, when subjected to curing, the same liquid composition sets to a solid form which can have a consistency comparable to that of a hard elastomeric rubber. The internal and external rheological control of polymer materials achieved by the present invention is believed to be of an extreme level, even for thixotropes. When subjected to shear force, the polymer composition is shear thinned and can flow more readily, perhaps comparably, to water.

The invention preferably employs a combination of: (i) mechanical pressure to shear thin and place a polymer composition into a porous web; (ii) an optional porous web pretreatment with a water repellent chemical, such as a

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fluorochemical, which is theorized to reduce the surface tension characteristics of the web and create a favorable surface contact angle between the polymer composition and the treated web which subsequently allows, under pressure and shear force exerted upon an applied polymer composition, the production and creation of an internal coating or layer which envelopes fibers or lines cell walls in a localized region within the web as a result of polymer flow in the web or which encapsulates the fibers within the web; and (iii) a polymer composition impregnated preferably having favorable rheological and viscosity properties which responds to such working pressures and forces, and is controllably placed into, and distributed in a web. This combination produces a web having the capability for a high degree of performance. This product is achieved through pressure controlled placement and applied shear forces brought to bear upon a web so as to cause controlled movement and flow of a polymer composition into and through a web. Preferably, repeated compressive applications of pressure or successive applications of localized shear forces upon the polymer in the web are employed.

By the preferred use of such combination, a relationship is established between the respective surface tensions of the polymer and the web, creating a specific contact angle. The polymer responds to a water repellent fluorochemical pretreatment of the substrate so as to permit enhanced flow characteristics of the polymer into the web. However, the boundary or edge of the polymer is moved, preferably repeatedly, in response to applied suitable forces into the interior region of a porous web so as to cause thin films of the polymer to develop on the fiber surfaces and to be placed where desired in the web.

Thixotropic behavior is preferably built into a polymer used in the invention by either polymer selection or design or additive/filler design. For example, it now appears that thixotropic behavior can be accentuated by introducing into a polymer composition certain additives that are believed to impart enhanced thixotropy to the resulting composition. A lower viscosity at high shear rates (during application to a web) is believed to facilitate polymer flow and application to a web, whereas a polymer with high viscosity, or applied at a low shear rate (before and/or after application) actually may retard or prevent structural element (including fiber) development or encapsulation.

Illustratively, the practice of this invention can be considered to occur in stages:

In stage 1, a silicone polymer composition impregnated is prepared. It can be purchased commercially and comes in typically two parts designated as A and B. For example, in a silicone polymer composition, as taught in U.S. Pat. No. 4,472,470, a base vinyl terminated polysiloxane is the A part, while a liquid organohydrogensiloxane controlled crosslinking agent is the B part. Certain remaining components, such as a resinous organopolysiloxane copolymer and a platinum catalyst may (or can) apparently initially be in either part A or part B.

Stage 2 can be considered to involve the mixing of such a product's parts with or without additives. Changes in viscosity can be obtained and measured based on applied shear rates and shear stresses. Such changes can be experienced by a polymer with or without additives. Up to a 99% reduction in viscosity of a liquid silicone polymer composition is believed to be obtainable by the shear forces involved in the shear thinning and forcing of a silicone polymer composition impregnated into a web. Thereafter, a very substantial increase in

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polymer viscosity is believed to be obtainable taking into account these same factors. Normally, the most significant factor is now believed to be the shear gradient that typically reduces the viscosity of the polymer below the starting or rest viscosity.

Stage 3 can be considered to be the pressure introduction stage. Up to a 99% reduction of the polymer viscosity is believed to be obtainable due to the applied shear forces, elapsed time, temperature, radiation and/or chemical changes. Thereafter, a significant increase or even more in the resulting polymer viscosity is believed to be obtainable. In this stage, partial curing of the polymer may take place. Most commonly, polymer viscosity is substantially decreased during the pressure controlled placement Stage 3 by the application of shear forces.

Stage 4 can be considered to be the first stage internal matrix dispersing and reintroduction with metering, and also recovery and recycle of excess polymer. Typically, within this Stage 4, the shear forces cause a substantial but temporary lowering of polymer viscosity, causing it to flow upon and into the three-dimensional structure of the web. The initial viscoelastic character of the polymer is typically theorized to be recovered almost immediately after shear forces are removed.

Stage 5 can be considered to be a second stage internal matrix dispersing and reintroduction with metering and also recovery and recycling of excess polymer. The variations in the viscosity of the polymer are equivalent to Stage 4. The viscosity of the polymer is again lowered causing it to flow within the web. Because of the application of repeated shear force induced reductions in viscosity, the thixotropic behavior of a polymer may not undergo complete recovery, following each application of shear force and the viscosity of the polymer may not revert to its original placement values. The polymer composition is believed to have the capacity to form enveloping internal coating in a predetermined region wherein the interstices or open cells are substantially completely filled within the three-dimensional matrix constituting a web during the time intervals that the is caused to flow under pressure in and about matrix components. In between these times, the polymer may recover substantially all of its initial high viscosity, although perhaps slightly less so with each repeated application of shearing pressure or force.

Stage 6 can be considered to be occurring just as curing is begun, and just as heat is introduced.

Stage 7 can be considered to be occurring with regard to the exertion of control of curing. Typically, at least a partial curing (including controlled cross-linking and/or polymerizing) is obtained by relatively low temperatures applied for relatively short times. For example, when light cotton, nylon, or similar fabrics are being treated, temperatures under about 350°, applied for under about 10 seconds, result in partial curing.

FIG. 8, consisting of FIGS. 8a through 8d, shows four graphs illustrating four ways that could be used for plotting polymer rheological behavior: (a) shear rate versus shear stress (uniform scales), (b) shear rate versus shear stress (log scales), (c) viscosity versus shear rate (uniform scales), and (d) viscosity versus shear rate (log scales), if desired, in the practice of this invention. Only the log versus log scales are believed to be capable of encompassing a full range of values for the three indicated variables. The graphs represent

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some broad ranges of viscosity changes relative to shear stress that could be undergone by a given silicone polymer composition during execution of a given pressured controlled placement procedure as taught herein.

For the purposes of the present invention, the term "surface tension" can be considered to have reference to a single factor consisting of such variables as intermolecular, or secondary, bonding forces, such as permanent dipole forces, induced forces, dispersion or nonpolar van der Waals forces, and hydrogen bonding forces. The strong primary bonding forces at an interface due to a chemical reaction are theorized to be excluded from surface tension effects; however, it is noted that even a small degree of chemical reactivity can have a tremendous influence on wetting effects and behavior affected by surface tension.

Surface tension is believed to induce wetting effects which can influence the behavior of a polymer composition impregnant relative to the formation of either a fiber enveloped layer therewith in a fibrous porous web, fiber encapsulation or both. For example, adhesion is theorized to be a wetting effect. Spontaneous adhesion always occurs for contact angles less than about 90°. However, for a combination of a rough surface and a contact angle over 90°, adhesion may or may not occur. In fact, roughness becomes antagonistic to adhesion, and adhesion becomes less probable as roughness increases.

Also, penetration is theorized to be a wetting effect. Spontaneous penetration occurs for contact angles less than about 90°, and does not occur for contact angles over about 90°. The roughness of a solid surface accentuates either the penetration or the repellency action, but has no influence on which type of wetting takes place.

In addition, spreading is theorized to be a wetting effect. Retraction occurs for contact angles over 90° or over planar surfaces for any contact angle. However, spontaneous spreading for contact angles less than 90°, especially for small contact angles, may be induced by surface roughness.

FIG. 9 is a schematic vector diagram illustrating the surface tension forces acting at the vertex boundary line of a liquid contact angle on a planar solid surface. It illustrates how surface tension forces might be measured between a silicone polymer composition and a fiber of a web (or a fabric) as treated by the invention.

FIG. 10 is a graph relating the contact angle over a smooth solid surface as a function of 0 and 1 that apply respectively, to adhesion ($i \cos \theta + 1$), penetration ($i \cos \theta$), and spreading ($i \cos \theta - 1$).

Regions of adhesion versus abhesion, penetration versus repellency, and spreading versus retraction are shown by shaded areas. FIG. 10 illustrates what is theorized to be the relationship of a silicone polymer composition to silicone polymer composition solids in a treated web as regards such factors as adhesion, penetration, spreading, and retraction.

FIG. 11, consisting of FIGS. 11a through 11d, shows representative viscosity profiles plotted on log viscosity versus log shear rate graphs for (a) pseudoplastic flow, (b) dilatant flow, (c) pseudoplastic flow with superimposed thixotropic behavior, and (d) laminar Newtonian flow that erupts into turbulent flow at a critical transition point.

FIGS. 11a through 11d show a broad range of illustrative flow characteristics that could be demonstrated by silicone polymer composition impregnants suitable for use in this invention using pressured controlled placement of a web as taught herein.

For purposes of this invention, the term "wetting" is used to designate such processes as adhesion, penetration, spreading, and cohesion. If wetting transpires as a sponta-

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neous process, then adhesion and penetration are assured when the solid surface tension exceeds the liquid surface tension. Surface roughness promotes these spontaneous wetting actions. On the other hand, no such generalizations can be made when the solid surface tension is less than the liquid surface tension.

Surface tension is measured as by S.T.L. units for liquid and by S.T.S. units for solids; both units are dynes/centimeter. When S.T.S. is less than S.T.L., then wetting is less ubiquitous and prediction of wetting behavior is more difficult. However, by taking advantage of the liquid/solid contact angle that forms when a liquid retracts over a solid, it is possible to calculate with reasonable accuracy the wetting behavior that can be expected. The reduction in liquid surface area can be computed in terms of the contact angle that the liquid makes with the solid surface. Contact angles are always measured in the liquid phase. There is a point of equilibrium where the surface tension forces become balanced.

By measuring the contact angle of a liquid on a solid, the wetting behavior of the liquid impregnant can be measured.

This invention is further illustrated by the following examples, which are not to be construed in any way as imposing limitations upon the scope thereof. On the contrary, it is to be clearly understood that resort may be had to various other embodiments, modifications, and equivalents thereof, which, after reading the description herein, may suggest themselves to those skilled in the art without departing from the spirit of the present invention and/or the scope of the appended claims.

EXAMPLES

Example 1

Liquid Silicone Polymer Preparation

100 parts by weight of the curable liquid silicone polymer available commercially from Mobay as "Silopren® LSR 2530" was mixed in a 1:1 ratio, as recommended by the manufacturer, A Hockmayer F dispersion blade at low torque and high shear was used to do the mixing. To this mixture were added 5 parts by weight of BSF "Uvinul 400" and 5/10 parts by weight Dow Corning 7127 accelerator, believed to be a polysiloxane but containing an undisclosed active accelerated ingredient.

Examples 2-19

Liquid Silicone Polymer Preparation

The procedure of Example 1 was repeated with various other curable viscous liquid silicone polymer compositions commercially available. To this product system is added a substituted benzophenone and other additives, the result of which are shown in Table II. All parts are by weight.

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TABLE II

Illustrative Silicone Resin Compositions					
EX.	STARTING SILICONE	MIXTURE RATIO OF PACKAGED	SUBSTITUTED BENZOPHENONE	OTHER ADDITIVES	
NO.	RESIN	COMPONENTS ¹	NAME	PARTS	PARTS
1	Silopren® LSR 2530	1:1	Uvinul 400	5	7127 Accelerator
2	Silastic® 595 LSR	1:1	Uvinul 400	5	Syl-Def® 7611 ⁽¹²⁾
3	SIL 5100 LiquidBC-10	10:1	Uvinul 400	5	Sylux® 2 ⁽¹³⁾
4	Silopren® LSR 2530	1:1	Uvinul 400	5	Hydral® 710 ⁽¹⁴⁾
5	Silopren® LSR 2530	1:1	Uvinul 400	5	Silopren® LSR Z3042 ⁽¹⁵⁾
6	SIL 5300	10:1	Uvinul 400	5	
7	Silopren® LSR 2540	1:1	Uvinul 400	5	
8	SIL 5300	10:1	Uvinul 400	5	
9	SIL 5106	10:1	Uvinul 400	5	
10	Silopren® LSR 2530	1:1	Uvinul 400	5	Fluorescing Agent OK412® (16)
11	Silopren® LSR 2530	1:1	Uvinul 400	5	Nalco® 15J-612 Colloidal Silica ⁽¹⁷⁾
12	Silopren® LSR 2530	1:1	Uvinul 400	5	Nalco® 15J-614 Colloidal Alumina ⁽¹⁸⁾
13	Silastic® 595 LSR	1:1	Uvinul 400	5	200 Fluid ⁽¹⁹⁾
14	Silopren® LSR 2530	1:1	Uvinul 400	5	
15	Silastic® 595 LSR	1:1	Uvinul 400	5	Zepel® 7040 ⁽²⁰⁾
16	Silastic® 595 LSR	1:1	Uvinul 400	5	Zonyl® UR ⁽²¹⁾
17	Silastic® 595 LSR	1:1	Uvinul 400	5	Zonyl® PSN-100 ⁽²²⁾
18	Silopren® LSR 2530	1:1	Uvinul 400	5	DLX-600® (11)
19	Silopren® LSR 2530	1:1	Uvinul 400	5	TE-3608® (14)

Table II Footnotes:

⁽¹⁾Ratio listed is that recommended by the manufacturer.⁽²⁾Syl-Def® (registered trademark of Dow Corning) is a crosslinker.⁽³⁾Sylux® 2 (registered trademark of W. R. Grace Co.) is a synthetic amorphous silica.⁽⁴⁾Hydral® 710 (registered trademark of Alcoa) is hydrazine aluminum oxide.⁽⁵⁾Silopren® LSR Z3042 (registered trademark of Mobay) is a silicone primer (bonding agent) mixture.⁽⁶⁾Fluorescing Agent OK412® (registered trademark of Degussa Corp.) is a zinc coated silica dioxide.⁽⁷⁾Nalco® 15J-612 Colloidal Silica (registered trademark of Nalco Chemical Company) is an aqueous solution of silica and alumina.⁽⁸⁾Nalco® 15J-614 Colloidal Alumina (registered trademark of Nalco Chemical Company) is an aqueous colloidal alumina dispersion.⁽⁹⁾200 Fluid (registered trademark of Dow Corning) is a 100 centistoke viscosity dimethylpolysiloxane.⁽¹⁰⁾Zepel® 7040 (registered trademark of duPont) is a nonionic fluoropolymer.⁽¹¹⁾Zonyl® UR (registered trademark of duPont) is an anionic fluorosurfactant.⁽¹²⁾Zonyl® PSN-100 (registered trademark of duPont) is a nonionic fluorosurfactant.⁽¹³⁾DLX-600® (registered trademark of duPont) is polytetrafluoroethylene micropowder.⁽¹⁴⁾TE-3608® (registered trademark of duPont) is a polytetrafluoroethylene micropowder.

Example 20

Internally Coated Fiber Encapsulated Interslice Filled Fabric Preparation

A complete, stepwise, application of the inventive method in the production of an encapsulated fiber fabric was as follows.

The selected base fabric was TACTEL® (gold color) #612071 available from ICI Americas, Inc. through their agent, Arthur Kahn, Inc. This fabric was 100% woven nylon. If desired, this and other fabrics may be considered to

modify surface texture. The fabric was weighed and measured. Its initial weight is 3.1 ounces per square yard. Its thickness equals 9 mils. The fabric was next washed with detergent, rinsed thoroughly, and hung to air dry. The fabric was soaked in water, wrung dry, and weighed. The water retained was equal to 0.8 g water/g fabric. The fabric was then treated with a water repellent fluorochemical, a 2% solution by weight of Zepel® 7040. In order to do so the fabric must be soaked in a 2.5% solution of Zepel® water-repellent chemical in distilled water. This was because:

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$$\frac{1 \text{ g fabric} - (0.02)}{0.8 \text{ g water}} = 0.025$$

The treated fabric was then run through a wringer and air dried. Next, the fabric was heated in an oven for 1 minute at 350°. This heating sinters the water repellent fluorocarbon. The fabric with its fluorocarbon residue is then run as in the FIG. 7 embodiment, in a vertical configuration and is described below. The fabric is run from a roll that incorporates significant braking or clutching to initiate the tension required for controlled material alignment and coating during application. The fabric web travels through a series of idler rolls ending at the application trough. As it passes the application trough, it picks up a thin coating of silicone impregnant and then moves under a shear blade that is parallel to the floor. The silicone impregnant is applied at 1.0 oz./sq. yd. and continues under a flex blade that is also parallel to the floor.

Multiple process stages of running the fabric with applied impregnant under the blades are preferably made. The multiple process stages are important, and are normally necessary. The impregnant is Mobay 2530 A/B in a 1:1 ratio and can be considered to be a viscoelastic liquid that flows only under the shear forces resulting from the pressured controlled placement. The impregnant is believed to return very substantially to its original viscous condition almost immediately upon release of the pressure. The impregnant was believed to flow a short distance within the matrix of the fabric during the short time that it was, because of pressure shearing forces, of lowered viscosity. Therefore, a number of "flows" may be usefully generated in a number of passes in order to properly distribute the impregnant in its preferred position substantially encapsulating the surfaces of the fabric's fibers.

Finally, the impregnated fabric was run through a line oven, of approximately 10 yards in length, at 4-6 yards per minute, and was cured at 325-350° F. It then passes through a series of idler rollers and is rolled up on a take-up roll, completing the tension zone. The resultant fabric has a non-tacky thin film of silicone that was internally coated to form a fiber encapsulated, interstice-filled layer in the fabric.

Example 21

Evaluation of Fiber Encapsulated Fabric Properties

The test results of the original versus the produced fiber encapsulated fabric of Example 20 were as follows:

TABLE III

FABRIC	ORIGINAL FABRIC	ENCAPSULATED
Spray Rating (1)	20	100 (reverse = 100)
Rain Test (2)	Fail	Pass
Abrasion Test (cycles) (3)	1,800	3,200
Moisture Penetration (4)	Saturated	0.0 g
Hydrostatic Resistance (psi) (5)	1	2
MVTR (g/m ² /day)* (6)	4.414	2.362
Weight (oz/yd ²)	3.1	4.1

Amount Impregnated = 1 + oz/yd²

*Environmental chamber at 104° F and 74% humidity.

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TABLE IV

LAUNDERING TEST	TIMES WASHED			
	Initial	5x	10x	15x
(Spray Rating)				
Impregnated Side	100	90	90	90
Reverse Side	100	90	90	90
Unimpregnated Treated Fabric	100	80	60	40

Accelerated Weathering Test (8)

Samples placed in QUV weatherometer for 72 hours.

Original=7

Impregnated Side=9

Reverse Side=8

- (1) The spray test was conducted in accordance with AATCC 22-1974. It measures water repellency of a fabric sample on a scale of 0-100, with a reading of 100 designating a completely water repellent fabric.
- (2) The rain test was conducted in accordance with AATCC 35-1985. It measures resistance of a fabric sample to penetration of water under static pressure from a shower head of 3 feet/5 minutes. A fabric is stormproof when less than 1.0 gram of water is absorbed by a standardized blotter used in the test.
- (3) The abrasion test was conducted in accordance with Federal Test Method Standard 191 A, Method S306. Abrasion resistance is measured by mounting a fabric sample on a Taber Abraser Model 174 and measuring the number of cycles before the fabric begins tearing apart.
- (4) The hydrostatic resistance test was conducted in accord with Federal Test Method Standard 191A, Method 3512. The test measures a fabric samples' resistance to water under pressure using the Mullen's Burst Test methods and apparatus. Test results are expressed in pounds per square inch at which water beads penetrate the fabric.
- (5) The moisture vapor transmission (MVTR) test was conducted in accordance with ASTM E96-B. The test measures the amount of moisture vapor passing through a fabric sample in a controlled environment during a 24 hour period. The obtained MVTR figure is expressed in grams of water/square meter of surface/24 hour day. The environmental chamber was held at 104° F and 47% humidity.
- (6) The moisture vapor transmission (MVTR) test was conducted in accordance with ASTM E96-B. The test measures the amount of moisture vapor passing through a fabric sample in a controlled environment during a 24 hour period. The obtained MVTR figure is expressed in grams of water/square meter of surface/24 hour day. The environmental chamber was held at 104° F and 47% humidity.
- (7) A laundering test of the conventional household type was performed. Fabric samples were washed with Tide® detergent. There was no drying. A spray test was subsequently carried out after each wash to determine the effect of the washing.
- (8) The accelerated weathering test was conducted in accordance with ASTM G-53. Samples of original and impregnated fabrics were placed in the weatherometer of QUV Company and results were compared. (All readings were based on a graduated color scale of 0-20; 10 designated the original color, while 0 designated a white out.)

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Example 22

Description of Fabric Controlled Placement Through Scanning Electron Microscope (SEM) Photomicrographs

FIGS. 3a, 3b and 3c were taken using a Cambridge 360 scanning electron microscope. The samples were cut using Teflon coated razor blades, mounted on 1/4 inch diameter aluminum stubs and coated with a gold/palladium alloy.

FIG. 3a is a photomicrograph of the gold color Tactel fabric described in Example 20. The surface of the material has been magnified 120 times and shows that the cured silicone polymer impregnant is present as a thin film, or coating, or layer within the material and envelopes at least a portion of the fibers. The fiber bundles are somewhat distinguishable in the weave, but each filament in the fiber bundles is not individually distinct.

The sample in FIG. 3b has been magnified 600 times and shows the cross-section of a fiber bundle from the same Gold Tactel in FIG. 3a. The cured silicone polymer impregnant envelopes at least a portion of the fibers. The interstices or void areas between filaments in the region of the internal coating are mostly filled or plugged by such impregnant. However, the web remains breathable and because of the impregnant barrier, is either water resistant or waterproof.

FIG. 3c is the side of the fabric in FIG. 1 opposite from which the silicone polymer impregnant was applied. The silicone polymer impregnant is most readily apparent at the fiber bundle interstices and not visible in the fiber bundles themselves.

Example 23

Fiber Enveloped Fabric Preparation

The selected base fabric was Arthur Kahn TACTEL® (hot coral) #70146. This fabric is 100% nylon. The fabric was pretreated at Cal-Pacific (a commercial finisher of fabric) with duPont ZEPHEL® 6700. The impregnant composition is Mobay LSR 2530 A/B in a 1:1 ratio-5% W UVINUL® 400 (5% of total weight of Mobay LSR). Controlled placement of this composition was performed in a three stage continuous process using equipment as shown in FIG. 7 consisting of the following procedure:

The composition was applied to the fabric at (a) a pressure of 3 lbs./linear inch, utilizing (b) a shear (bar) knife at a high pressure, and at a 90° angle to the fabric (the edge of the knife is milled sharp). The rate of application is at approximately 1.0 oz./sq. yd. A flex knife was then applied at a 45° angle with the recovery system utilizing gravity. For both (a) and (b) above, the microweb pressure was applied at a low web speed on a roller system varied at from about 260-400 yards per hour. Next, the fabric is cured using an upper oven (lower oven turned off) at a temperature of about 320-330° F. The fabric was in the oven for approximately 3 to 4 minutes. The impregnant cures in a non-tacky thin film, as in the previous example.

Example 24

Prior Art Silicone Polymer Treated Fabric

The fabric resulting from a prior art application of a viscous liquid curable silicone polymer composition is shown in FIG. 2. The photographic view of FIG. 2 is at 150x magnification. It shows a polyester and cotton cloth blend into which Dow Corning 590 LSR silicone polymer composition has been coated by a procedure of the prior art. The fabric side shown in FIG. 2 is the top, or treatment, side, which was the fabric side upon which coating was accomplished.

As shown by the example of the treated fabric of FIG. 2, the prior art impregnated fabric is characterized by a high degree of disorder. A large number of particulates (typical)

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appear to litter the surface of the fabric. A substantial portion of the area of the surface, which appears to be a solid layer, is silicone polymer composition. Certain yarn fragments can be observed to protrude through the surface of this silicone polymer composition. Additionally, the silicone polymer composition on either the polyester or the cotton fibers, is not an encapsulation layer, but rather a matrix with the coated fibers being in general disarray, probably from forces occurring during the indicated prior art silicone polymer composition application procedure. Although silicone polymer composition is present upon the yarn or fiber surfaces of the substrate, and certainly is present as a layer upon the exterior surface of the three-dimensional fabric body, the silicone polymer composition has not controllably and individually encapsulated the fibers and left the interstices between fibers largely devoid of such polymer. In the prior art, a placement of silicone polymer composition in a fabric is not controlled to such a degree so as to produce a product in accordance with the present invention.

Example 25

Description of Fabric Controlled Placement Through Scanning Electron Microscope (SEM) Photomicrographs

FIGS. 13a, 13b and 13c were taken using a Cambridge 360 scanning electron microscope. The samples are cut using Teflon coated razor blades, mounted on 1/4 inch diameter aluminum stubs, and coated with a gold/palladium alloy.

FIG. 13a is a photomicrograph of the Tactel (Hot Coral) fabric described in Example 23. The surface of the material has been magnified 120 times and shows that the cured silicone polymer impregnant is present as a thin film, or coating, or layer within the material and envelopes at least a portion of the fibers. The fiber bundles are somewhat distinguishable in the weave, but each filament in the fiber bundles is not individually distinct.

The sample in FIG. 13b has been magnified 800 times and shows the cross-section of a fiber bundle from the same Tactel in FIG. 13a. The cured silicone polymer impregnant envelopes at least a portion of the fibers. The interstices or void areas between filaments in the region of the internal coating are mostly filled or plugged by such impregnant. However, the web remains breathable and because of the impregnant barrier is either water resistant or waterproof.

FIG. 13c is the side of the fabric in FIG. 1 opposite from which the silicone polymer impregnant was applied. The silicone polymer impregnant is most readily apparent at the fiber bundle interstices and not visible in the fiber bundles themselves.

FIG. 15a depicts a 330 denier cordura fiber, encapsulated with a composite polymer, magnified 1950 times. The left side of the picture is in normal scanning electron mode and the right side of the picture is magnified 10 times in secondary electron microscopy back scatter mode. The isolated rectangular box image in the middle of the left side was exposed to destructive electron beams isolated on the central opening in the center of the wrinkled formation. The wrinkled film casing represents the composite polymer (solid silicone and oxyethylated nylon) thin-film, this is a direct result of the destructive electron exposure. The image on the left side of the picture has surrounding fibers on the left and right side of the isolated fiber, which also has some wrinkled effects on the thin-film as a direct result of the destructive electron analysis. The rectangular box on the upper side of the picture was targeted for an elemental analysis. The electron beam was targeted at the rectangular box with very low current (10 KV and probe at 3.0 nA) to insure isolation of elemental signal from any other area. FIG. 15b depicts the elemental graph of the targeted region,

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which clearly shows the presence of the composite polymer containing si or silicon. Combined, FIGS. 15a and 15b show fiber encapsulation by the composite polymer.

FIG. 15c depicts a cut end of a filament illustrating a thin film encapsulation in white. A crack was created in the filament with a high temperature electron beam. This crack continues under the surface of the thin film. The filament has been cut and the thin film has been stretched or elasticized by the cutting of the filament. The two arrows in the upper right corner show the thickness or distance represented by the black box in the lower right corner as 126 nm.

FIG. 15d depicts an isolated image on 330 Denier Cordura single filament fiber processed with the micro-finish fiber coating technology, magnified 3,720 times. The Bioengineered Comfort™ polymer containing engineered protein and solid silicone was used in the process with a moderate degree of shear. The image on top of the fiber is an undispersed protein polymer which clearly illustrates the presence of the protein after the micro-finish fiber coating process. The surface morphology has very small protein polymer particles encapsulated in the solid silicone polymer and is homogeneously dispersed throughout the film system on the fiber.

FIG. 15e is an image of a white nylon magnified 178 times. The application side is shown at the bottom left hand corner of the image. The upper portion of the image is the non-application side. At the upper right corner is the intersection of the warp and fill fiber bundles, where the polymer presence can clearly be seen on the fibers. The internal layer of polymer that creates the liquid barrier or resistant property can be seen along the bottom right corner of the picture. This internal layer is a combination of polymer filling some interstitial spaces and polymer "glueing" together the fibers and filaments of the web.

FIG. 15f is a Tunneling Electron Microscopy (TEM) image of a thin cross section of a filament encapsulated with polymer. The lighter image on the lower side of the frame is a polyester filament. The black spherical dots on the outer edge of the fiber are extremely dense processed material. In this imaging technique, the darker the image, the denser that specific material.

FIG. 15g depicts an individual filament shown in a split screen format. The left hand image is showing the filament with submicron metal particles dispersed in the processed film. The right hand portion of the split screen is imaging the filament with a technique known as secondary electron back scattering. The bright particles are the same particles on the same fiber as seen in the left side of the split screen. The difference is one of density, the brighter metal particles are imaging density differential over the underlying filament.

FIG. 15h depicts a nylon fabric magnified 419 times with bright particle tracer images and a cross sectional image of a nylon fabric. These bright particles are submicron metal particles dispersed throughout the fabric in the processed film. The addition of bright copper submicron particles in the polymer allows secondary back scatter mode to illustrate the complete encapsulation ability of the controlled placement technology. The left side of the image is the performance side of the fabric which is the non-application side of the polymer, but it is clear, with the presence of the glowing brightness of the copper submicron particles throughout the performance side of the fabric, that controlled placement technology successfully encapsulates completely around the fibers throughout the fabric structure. The other clear unique feature of the controlled placement technology is that each fiber is still independent. This differentiation allows the controlled placement technology's processed fabrics to

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retain exceptional hand and tactile quality, while still imparting performance characteristics. On the left side of the fabric, directly underneath the printed text "performance side", an elemental analysis was conducted and the outcome of that analysis is depicted in FIG. 15i. The result clearly shows a strong presence of submicron copper particles.

In the next examples that involve accelerated weathering, abrasion, water repellency, moisture penetration, and rain testing, data is provided for a Tactel fabric identified as Deva Blue. The fabric is 100% nylon, available from Arthur Kahn and identical in composition, preparation, and enveloping specification to that of the Hot Coral presented in previous examples.

Example 26

Accelerated Weathering Test

The results of weathering upon a treated web of this invention are shown in actual tested sample pieces comparing original fabrics with embodiments of the enveloped fiber fabrics of this invention.

In every case, the enveloped fiber fabric samples were found to have significantly better weathering characteristics than the original untreated fabrics as determined by accelerated weathering tests. Even the reverse side (compared to the treated side) of an enveloped fiber nylon fabric of the Tactel® type was improved over the original fabric. In addition, the excellent "hand" of the enveloped fiber fabric was found to have been maintained after the accelerated weathering test.

The test performed conforms to each of the following performance standards:

- ASTM G-53 light/water exposure materials
- ASTM D-4329 light/water exposure-plastics
- General Motors Test spec TM-58-10
- ISO 4892 Plastics exposure to lab light

The procedure used for the accelerated weathering testing involved subjecting fabric samples in four hours of high-intensity ultraviolet light, alternating continuously with four hours of water condensation, wetting the fabric in the dark. This alternating exposure (four hours on, four hours off) to high-intensity ultraviolet light and water wetting, simulates outdoor environmental conditions in a vastly accelerated manner, quickly degrading unprotected dyes and fibers. The methods and apparatus used for this test was a QUV Accelerated Weathering Tester from The Q-PANEL Company, 26200 First Street, Cleveland, Ohio 44145.

The results obtained on some sample fabrics are expressed in Table V. In this Table, results are expressed in the form of "A/B" where A and B are numbers. The number "A" is the color rating on a graduated scale from 0 to 10. The number 10 equals perfect (original) condition where 0 equals a white color and a completely faded fabric. The number "B" is the number of hours of weathering transpiring when the number "A" rating was obtained.

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TABLE V

Accelerated Weathering Testing				COLOR RATING (RATING/HOURS) 10 - PERFECT 0 - WHITE FADES OUT
ORIGINAL FABRIC	ORIGINAL FABRIC WEATHERED	ENVELOPED FABRIC WEATHERED	REVERSE SIDE WEATHERED	
TACTEL® Davy Blue 9-420-6-1				After 159 hrs., enveloped fabric significantly less weathered than original; original nearly white; enveloped fabric still light blue.
10/0	3/159	8/159		
TACTEL® Hot Coral 9-420-6-2 (AKA 18)				After 24 hrs., enveloped fabric is significantly less weathered than original, as was reverse side.
10/0	5/24	10/24	9/24	

Example 27

Abrasion Resistance Testing

The results of abrasion resisting testing clearly show that enveloped fiber fabrics of this invention have superior wear characteristics compared to the untreated original (starting) fabrics. In most cases, the enveloped fiber fabric samples underwent twice as many cycles as the untreated samples without evidencing tearing in the samples. Such results can be explained by theorizing that the envelopment with silicone polymer of the yarns and fibers comprising a fabric, provides such treated yarns and fibers with a lubricity agent so that abrasive action was minimized and the integrity of the fabric was preserved significantly longer. The anti-abrasion characteristics also applied to the minimized effects of one fiber rubbing against another fiber, or of one yarn against another yarn.

This experiment compared the abrasion resistance of embodiments of the enveloped fiber fabrics of this invention with untreated fabrics. The durability of each fabric test specimen was determined by the Taber Abraser. Each specimen is abraded for the number of cycles indicated. Comparisons were then made between the enveloped fiber fabrics of the invention and untreated fabrics. Specifically, this test method utilizes the Taber Abraser No. 174. An important feature of this abrader was that its wheels traverse a complete circle on the test specimen surface. Thus, the surface was abraded at all possible angles relative to the weave or grain of the specimen. Comparisons of the enveloped fiber fabric to the untreated fabric were based upon a scale 0 through 10, where 0 was a completely torn specimen, and 10 was the new (or starting) sample.

Each test procedure used a single 7 inch diameter fiber enveloped fabric specimen, and a single 7 inch diameter original (untreated) fabric specimen. The procedure used was as follows:

1. A test specimen of the fiber enveloped fabric with a 7 inch diameter was cut.
2. An equally-sized specimen of control (untreated) fabric was cut.
3. The fabric specimen was mounted on the rotating wheel securely and the clamps were screwed down.
4. The counter was set.
5. The vacuum power adjustment was set. (For this experiment, vacuum was set at 80.)
6. The abraser was started.
7. At the procedurally specified number of revolutions, the abraser was stopped and each fabric sample was rated at a value between 0 and 10.

20 Illustrative results of the test on some sample fabrics are shown in Table VI.

Abrasion Testing

Numeric Grade of Abrasion 0-10

- 0—Total failure of fabric specimen. Fibers are torn apart
5—Fabric specimen is starting to tear. Fabric is noticeably thinner
10—Original unabraded fabric specimen

TABLE VI

SPECIMENS	UNTREATED FABRIC	ENCAPSULATED FABRIC	COMMENTS
Hot Coral Tactel	5 1,000 cyc.	7 1,000 cyc.	Untreated sample is starting to tear, and enveloped sample was still intact.
Davy Blue Tactel	4 1,000 cyc.	7 1,000 cyc.	Visible rips in untreated sample. Enveloped sample fibers were frayed.

Example 28

Breathability Testing

This test procedure followed the Modified ASTM E96-8 test. As shown by the results of this testing in the following Table, the fiber enveloped fabrics of this invention were found to have high breathability. This breathability was in excess of that needed to remove the average value of several thousand grams of perspiration generated daily by the human body. The results for the fiber enveloped fabrics of this invention were generally superior to the corresponding results measured under the same conditions for prior art treated fabrics, such as the Gore-Tex® brand fabric.

Breathability of a fabric sample was determined by accurately weighing the amount of water passing through such fabric sample under carefully controlled temperature and relative humidity conditions in an environmental chamber. The water weight loss from a cup whose mouth is sealed with a fabric sample was expressed as grams of water vapor per square meter of fabric per 24 hour day.

In an attempt to more realistically simulate what is actually occurring inside the apparel during exercise, a

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specially designed test was performed to measure outward water vapor transport (MVTR) in a "Bellows" effect. The test simulates the high volumes of moisture and air that mix within a garment that pass outward through it as air is drawn in resultant from activity. The enveloped fabrics of this invention were found to provide increased performance at a higher activity, or air exchange level than is achievable with corresponding untreated fabrics.

The "Bellows" MVTR breathability test was run inside of a controlled temperature/humidity chamber similar to the foregoing cup test. However, instead of a standard cup, each fabric sample was sealed over the open top of a special cup which was provided with an air inlet aperture in its bottom, thereby allowing air to be bubbled up through the sealed container at a controlled rate. A check valve at the air inlet operation prevents backup or loss of water from the container. The air bubbles passed upwardly through the water and out through the fabric sample mounted sealingly across the cup top along with the water vapor. Table VII illustrates some representation results obtained.

TABLE VII

Moisture Vapor Transport (MVTR)	
FABRIC	MVTR ⁽¹⁾
Made by a Method of the Invention	13,600
Enveloped fiber fabric, Hoi Chai Trade	
Commercial Products	10,711
Omni-Tex (3)-Ply Fabric	

Table Footnote:

⁽¹⁾MVTR here referenced minimum vapor transport through a fabric sample as measured by the "Bellows" test with air delivered to the bubbler at 2 to 4 psi air pressure, in an Environmental Chamber at 100 to 102° F. and 36-42% relative humidity. MVTR is expressed as grams of water per square meter of surface per 24 hour day.

Example 29

Water Repellency: Spray Testing

Water repellency spray testing is carried out according to AATCC Test Method 22-1974. The results of such testing show that the fiber enveloped Tactel®-type fabrics of the invention show excellent initial spray ratings initially, as do the original untreated fabrics which have been treated with water repellent chemicals such as fluorochemicals. Specifically, as the results shown below demonstrate, after ten machine washes, the treated side of a fiber enveloped fabric of the invention was found to remain highly water repellent, while, on the reverse side thereof, the original water repellency rating was found to have fallen significantly. The water repellency spray rating on the untreated fabric fell even more drastically. Excellent "hand" was retained after the test. It is believed that pretreatment with a fluorochemical having good water repellent properties can augment and even synergistically coact with the silicone resin used to produce fiber enveloped fabrics of this invention to produce superior spray ratings in such a fiber. The results are shown in Table VIII.

This test method is believed to be applicable to any textile fabric, whether or not it has been given a water resistant or

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water-repellent finish. The purpose of the test is to measure the resistance of fabrics to wetting by measuring the water-repellent efficiency of finishes applied to fabrics, particularly to plain woven fabrics. The portability and simplicity of the instrument, and the shortness and simplicity of the test procedure, make this method of test especially suitable for mill production control work. This test method is not intended, however, for use in predicting the probable rain penetration resistance of fabrics, since it does not measure penetration of water through the fabric.

The results obtained with this test method are believed to depend primarily on the resistance to wetting, or the water repellency, of the fibers and yarns comprising a fabric, and not upon the construction of the fabric. This test involves spraying water against the taut surface of a test fabric specimen under controlled conditions which produce a wetted pattern whose size depends on the relative water repellency of the fabric. Evaluation is accomplished by comparing the wetted pattern with pictures on a standard chart. The methods and apparatus and materials employed for this test were an AATCC Spray Tester, a beaker, distilled water, and the specimen fabrics.

The procedure followed for this test was as follows: a test specimen, which had been conditioned as procedurally directed, was fastened securely in a 15.2 cm (6") metal hoop so that it presented a smooth wrinkle-free surface. The hoop was then placed on the stand of the tester so that the fabric was uppermost in such a position that the center of the spray pattern coincided with the center of the hoop. In the case of twills, gabardines, piques or fabrics of similar ribbed construction, the hoop was placed on the stand in such a way that the ribs were diagonal to the flow of water running off the fabric specimen.

250 milliliters (ml) of distilled water at 27° C. (80° F. ± 2° F.) was poured into the funnel of the tester and allowed to spray onto the test specimen, which took approximately 25 to 30 seconds. Upon completion of the spraying period, the hoop was taken by one edge and the opposite edge tapped smartly once against a solid object, with the fabric facing the object. The hoop was then rotated 180 degrees and then tapped once more on the location previously held.

The procedure and methods and apparatus of this test were slightly modified from the specifications, as follows:

1. The spray nozzle holes were slightly larger than specified, but the flow rate of the nozzle was 250 ml/30 sec., as required.

2. The number of taps of the hoop was two instead of one.

For each wash test, a fabric sample was washed using a warm wash/cold rinse cycle with one cup of Tide® detergent and dried at a hot/dry cycle in a dryer, unless otherwise indicated. The test results were evaluated by comparing the wet or spotted pattern on the fabric sample after tapping the hoop with the standard rating chart. Results produced surface wetting, with no water completely soaking through the test fabric sample. The numbers were ratings based upon the standard chart. Such values are thus subjective deductions by an experienced experimenter.

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TABLE VIII

Spray Test Results

ORIGINAL FABRIC	ENVELOPED FIBER FABRIC OF THE INVENTION							
	Initial				After 5 Washes		After 10 Washes	
Total #	Initial	After 5 Washes	Enveloped Side	Reverse Side	Env Side	Reverse Side	Env Side	Reverse Side
Devco Blue 9-420-A-1	100	10	90	100	90	70	80	50
Hot Coral 9-420-B-2	100	30	90	100	70	55	70	30
Gold Tinsel 8-100-1	100	100	90	90	90	90	90	90

Example 30

Moisture Penetration Test

The results shown in the Table below demonstrate that all of the fiber enveloped fabrics of this invention test were significantly better than the original untreated fabrics with regard to resisting the penetration of water under the test conditions used after the test, the "hand" of the tested fabric samples remained excellent.

The purpose of this test was to evaluate how well a fabric stands up to wetness under continuous pressure, such as kneeling on the ground, or sitting in a wet chairlift, for a period of 30 minutes. This test involves placing both a fabric sample and a standard blotter sample on top of a water

1. The fabric sample was placed with one side facing the water.
2. One piece of dry blotter paper was placed over the fabric to cover the pan.
3. Scrap fabric was placed over the blotter paper to cushion the weight.
4. The 87 lb. weight was distributed evenly over the 100-square-inch area.
5. This assembly was left undisturbed for 30 minutes.
6. After this time period, the visual results were recorded.

TABLE IX

Fiber Enveloped Fabric of the Invention

FABRIC SAMPLE AND THICKNESS	ENVELOPED SIDE OF FABRIC FACTNO WATER	NON-ENVELOPED SIDE OF FABRIC FACTNO WATER	CONTROL FABRIC
Devco Blue Tinsel # 0.009 microns	No water penetration through the fabric. No visible water spots. Paper weight = 4.7 gm Water gain = 0.0 gm	No water penetration through the fabric. No visible water spots. Paper weight = 4.7 gm Water gain = 0.0 gm	Failure - total saturation of fabric and blotter

container which contains 700 ml of tap water. The fabric sample and the blotter sample are each then subjected to a continuous pressure of 87 lbs. distributed evenly over 100 square inches of surface area for a period of 30 minutes. After this time, a visual inspection of the fabric is made for any water penetration, and the paper blotter is weighed to detect water gain or penetration.

The methods and apparatus employed for each such test was one 20 inch diameter aluminum pan, one 87 lbs. weight distributed evenly over 100 square inches of fabric, one paper blotter, 700 ml water, miscellaneous fabric scraps for cushioning and the test fabric sample pieces.

Paper blotter dry weight: 4.7 gm

Total weight applied to fabric: 87 lbs.

Pressure evenly distributed over surface area of: 100 sq. in.

Pressure: 0.87 lbs./sq. in.

The procedure observed for this test was as follows:

1. 700 ml tap water was placed in the round pan.

Example 31

Rain Test

In this testing, the rain test procedure of AATCC Method 35-1985 was followed.

The rain test results obtained demonstrate the clear superiority of the fiber enveloped fabric of the present invention as compared to the original untreated fabric. The data in the Table below shows that fiber enveloped fabrics pass this test by allowing virtually no water to pass therethrough. This result is comparable to the results obtained with higher cost so-called breathable waterproof fabrics currently commercially available in the market. In contrast, the original, untreated fabrics fail to pass this test because they demonstrate complete saturation. The fiber enveloped fabric samples retain excellent "hand" after the test.

The purpose and scope of this ASTM test is to evaluate resistance of a fiber enveloped fabric to water under simulated storm conditions. The test specifies that a test fabric is stormproof if less than one gram of water is absorbed by blotter paper with a shower head pressure of 3 feet exerted for 5 minutes. This test method is applicable to any textile fabric, whether or not it has a water repellent finish. It measures the resistance of a fabric to the penetration of

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water by impact, and thus can be used to predict the probably rain penetration resistance of a fabric. The results obtained with this method of test depend on the water repellency of the fibers and yarns in the fabric tested, and on the construction of the fabric.

This test involves a test specimen backed by a pre-weighed standard blotter. The assembly is sprayed with water for 5 minutes under controlled conditions. The blotter then is separated and weighed to determine the amount of water, if any, which has leaked through the specimen fabric during the test and has been absorbed by the blotter.

The methods and apparatus and materials employed in each test were a modified rain tester, blotter paper, water at 80° F.±2° F., a laboratory balance, 8"x8" fabric specimens which had been pre-conditioned in an atmosphere of 65% (±2%) relative humidity and 70° F (±2° F) for four hours before testing, and tape.

The procedure followed for this test was as follows:

1. A 6"x6" paper blotter was weighted to the nearest 0.1 gm and placed behind the test specimen.
2. The test fabric with the paper blotter in registration therewith was taped on the specimen holder.
3. A tube in the rain tester was filled with water up to the 3 foot level. It was confirmed that water was flowing out of the overflow tube which maintains the 3 foot column of water.
4. The water spray distance from the tip of the nozzle to the specimen holder was measured and adjusted to 12 inches.
5. The specimen holder was left in place and the rain tester was turned on for five minutes.
6. After the test period, the paper blotter was removed and reweighed to the nearest 0.1 gm.

The results of the test selected fabric samples are shown in Table X.

TABLE X

Rain Test Results of Water Penetrating the Fabric.

FABRIC SAMPLE	ORIGINAL NOT WASHED	AFTER 5 MACHINE WASHES	AFTER 10 MACHINE WASHES
Hot Coral Tactel®	0	0	0
Deva Blue Tactel®	0	0	0
Prior Art Treated Fabrics			
Ultrex®	0	—	0.1
Gore-Tex®	0	0	—

Original Fabrics—Water Repellent Chemicals Only, No Encapsulation

Hot Coral Tactel/Failed-saturated; Deva Blue Tactel/Failed-saturated

It should be understood, of course, that the foregoing relates only to preferred embodiments of the present invention and that numerous modifications or alterations may be made therein without departing from the spirit and the scope of the invention as set forth in the appended claims.

What is claimed is:

1. A porous web comprising a three dimensional structure of a plurality of structural elements with interstitial spaces therebetween;

said web having a three dimensional top surface opposed from a three dimensional bottom surface;

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at least some of said structural elements of said top and bottom surfaces are encapsulated by a cured, liquid silicone polymer composition; and most of the interstitial spaces are open.

2. The web of claim 1 wherein most of the structural elements are encapsulated.

3. The web of claim 1 wherein substantially all of the interstitial spaces are open.

4. The web of claim 1 wherein substantially all of the structural elements are encapsulated.

5. The web of claim 1 wherein substantially all of the interstitial spaces are open.

6. The web of claim 4 wherein the thickness of the encapsulation on the structural elements of said top surface is greater than the thickness of the encapsulation on the structural elements of said bottom surface.

7. The web of claim 1 wherein substantially all of the interstitial spaces are open.

8. The web of claim 1 wherein the structural elements are fibers.

9. A porous web comprising a three dimensional structure of a plurality of structural elements with interstitial spaces therebetween;

most of said structural elements are encapsulated by a cured, liquid silicone polymer composition; and most of the interstitial spaces are open.

10. The web of claim 9 wherein substantially all of the structural elements are encapsulated.

11. The web of claim 10 wherein the thickness of said encapsulating polymer composition varies from one surface of said web to the other.

12. The web of claim 11 wherein the thickness of the encapsulation on the structural elements on the application side of said web is greater than the thickness of the encapsulation on the structural elements on the other side of said web.

13. The web of claim 9 wherein substantially all of the interstitial spaces are open.

14. The web of claim 13 wherein substantially all of the structural elements are encapsulated.

15. The web of claim 9 wherein the structural elements are fibers.

16. The web of claim 15 wherein said web is a fabric comprising warp yarns and fill yarns, each warp yarn and fill yarn including a plurality of fibers.

17. The web of claim 15 wherein the quantity of said polymer composition is in the range of about 5 to about 200 weight percent of the weight of the untreated web.

18. The web of claim 17 wherein the quantity of said polymer composition is in the range of about 20 to about 30 weight percent of the weight of the untreated web.

19. The web of claim 9 wherein said web is selected from the group consisting of polyolefins, polyamides, polyesters, regenerated cellulose, cellulose acetate, rayons, acetates, acrylics, aramids, azlons, glasses, modacrylics, novoloids, nylons, sarans, spandex, vinyl, vinylon, nylon, cotton, wool, silk, linen, jute, and mixtures thereof.

20. The web of claim 9 wherein said web comprises a laminate of a fabric and a non-woven porous substrate.

21. The web of claim 9 wherein said web comprises a laminate of a woven substrate and a non-woven substrate.

22. The web of claim 9 wherein said web comprises a laminate of more than one porous substrate.

23. The web of claim 9 wherein said polymer composition is selected from the group consisting of silicones, fluorosilicones, modified polyurethane silicones, and modified silicone polyurethanes.

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24. The web of claim 9 wherein said structural elements have been treated with a fluorochemical prior to encapsulation with said polymer composition.

25. The web of claim 24 wherein the quantity of said fluorochemical is in the range of about 0.01 to about 5 weight percent of the total weight of the untreated web.

26. The web of claim 25 wherein the total weight of said fluorochemical and said polymer composition is in the range of about 5 to about 200 weight percent of the total weight of the untreated web.

27. The web of claim 26 wherein the total weight of said fluorochemical and said polymer composition is in the range of about 10 to about 100 weight percent of the total weight of the untreated web.

28. The web of claim 9 wherein the thickness of said polymer composition encapsulating said structural elements ranges from about 0.01 to about 50 microns.

29. The web of claim 28 wherein the thickness of said polymer composition encapsulating said structural elements ranges from about 0.05 to about 5 microns.

30. The web of claim 9 that is characterized by having:
a water drop contact angle in the range of about 90° to about 160°;

a spray rating of at least 90 prior to washing;

a spray rating of at least 80 after 10 washes;

a passing rain test rating;

an increase in abrasion resistance of at least about 50% when compared to an untreated web;

a moisture penetration less than about 0.5 grams;

a hydrostatic resistance of at least 1 psi;

a moisture vapor transport rate of at least 35% of the untreated web; and

an accelerated weathering test rating of at least about 8.

31. The web of claim 9 that is characterized by having a spray rating of at least about 80 after 10 washes.

32. The web of claim 31 that is characterized by having a spray rating of at least about 80 after 15 washes.

33. The web of claim 9 that is characterized by having an increase in abrasion resistance of at least about 75% when compared to an untreated web.

34. The web of claim 9 that is characterized by having a moisture vapor transport rate of at least about 50% of the untreated web.

35. The web of claim 9 that is characterized by having a moisture penetration less than about 0.5 grams.

36. The web of claim 9 that is characterized by retaining most of the original hand of the untreated web.

37. A porous web comprising a three dimensional structure of a plurality of structural elements with interstitial spaces therebetween;

said web having a three dimensional top surface opposed from a three dimensional bottom surface;

a substantially continuous region of a cured, liquid silicone polymer composition extending through the web, said region of polymer composition filling the interstitial spaces and adhering adjacent structural elements; at least some of the structural elements above and below said region are encapsulated by a cured, liquid silicone polymer composition; and

most of the interstitial spaces between said encapsulated structural elements above and below said region are open.

38. The web of claim 37 wherein most of the structural elements above and below said region are encapsulated.

39. The web of claim 38 wherein substantially all of the interstitial spaces between said encapsulated structural elements above and below said region are open.

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40. The web of claim 37 wherein substantially all of the structural elements above and below said region are encapsulated.

41. The web of claim 40 wherein substantially all of the interstitial spaces between said encapsulated structural elements above and below said region are open.

42. The web of claim 37 wherein substantially all of the interstitial spaces between said encapsulated structural elements above and below said region are open.

43. The web of claim 37 wherein the thickness of said encapsulating polymer composition varies above and below said region.

44. The web of claim 43 wherein the thickness of the encapsulation on the structural elements above said region is greater than the thickness of the encapsulation below said region.

45. The web of claim 37 wherein the structural elements are fibers.

46. The web of claim 45 wherein said web is a fabric comprising warp yarns and fill yarns, each warp yarn and fill yarn including a plurality of fibers.

47. The web of claim 45 wherein the quantity of said polymer composition is in the range of about 5 to about 200 weight percent of the weight of the untreated web.

48. The web of claim 47 wherein the quantity of said polymer composition is in the range of about 20 to about 30 weight percent of the weight of the untreated web.

49. The web of claim 37 wherein said web is selected from the group consisting of polyolefins, polyamides, polyesters, regenerated cellulose, cellulose acetate, rayons, acetates, acrylics, aramids, azlons, glasses, modacrylics, copolymers, nitrils, sarans, spandex, vinyl, vinyon, nylon, cotton, wool, silk, linen, jute, and mixtures thereof.

50. The web of claim 37 wherein said web comprises a laminate of a fabric and a non-woven porous substrate.

51. The web of claim 37 wherein said web comprises a laminate of a woven substrate and a non-woven substrate.

52. The web of claim 37 wherein said web comprises a laminate of more than one porous substrate.

53. The web of claim 37 wherein said polymer composition is selected from the group consisting of silicones, fluorosilicones, modified polyurethane silicones, and modified silicone polyurethanes.

54. The web of claim 37 wherein said structural elements have been treated with a fluorochemical prior to encapsulation with said polymer composition.

55. The web of claim 54 wherein the quantity of said fluorochemical is in the range of about 0.01 to about 5 weight percent of the total weight of the untreated web.

56. The web of claim 55 wherein the total weight of said fluorochemical and said polymer composition is in the range of about 5 to about 200 weight percent of the total weight of the untreated web.

57. The web of claim 56 wherein the total weight of said fluorochemical and said polymer composition is in the range of about 10 to about 100 weight percent of the total weight of the untreated web.

58. The web of claim 37 wherein the thickness of said polymer composition in said region and encapsulating said structural elements ranges from about 0.01 to about 50 microns.

59. The web of claim 58 wherein the thickness of said polymer composition in said region and encapsulating said structural elements ranges from about 0.05 to about 5 microns.

60. The web of claim 37 that is characterized by having:
a water drop contact angle in the range of about 90° to about 160°;

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a spray rating of at least 90 prior to washing;
a spray rating of at least 80 after 10 washes;
a passing rain test rating;
an increase in abrasion resistance of at least about 50%
when compared to an untreated web;
a moisture penetration less than about 0.5 grams;
a hydrostatic resistance of at least 1 psi;
a moisture vapor transport rate of at least 35% of the
untreated web; and
an accelerated weathering test rating of at least about 8.
61. The web of claim 37 that is characterized by having
a spray rating of at least about 80 after 10 washes.
62. The web of claim 61 that is characterized by having
a spray rating of at least about 60 after 15 washes.
63. The web of claim 37 that is characterized by having
an increase in abrasion resistance of at least about 75% when
compared to an untreated web.
64. The web of claim 37 that is characterized by having
a moisture vapor transport rate of at least about 50% of the
untreated web.
65. The web of claim 37 that is characterized by having
a moisture penetration less than about 0.5 grams.
66. The web of claim 37 that is characterized by retaining
most of the original hand of the untreated web.

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67. A porous web comprising a three dimensional struc-
ture of a plurality of structural elements with interstitial
spaces therebetween;
said web having a three dimensional top surface opposed
from a three dimensional bottom surface;
a substantially continuous region of a cured, liquid sili-
cone polymer composition extending through the web,
said region of polymer composition filling the intersti-
tial spaces and adhering adjacent structural elements;
most of the structural elements of the top surface exposed
out of said region are encapsulated by a cured, liquid
silicone polymer composition; and
most of the interstitial spaces between said encapsulated
structural elements are open.
68. The web of claim 67 wherein substantially all of the
structural elements of the top surface exposed out of said
region are encapsulated.
69. The web of claim 67 wherein substantially all of the
interstitial spaces between said encapsulated structural ele-
ments are open.
70. The web of claim 69 wherein substantially all of the
structural elements of the top surface exposed out of said
region are encapsulated.

* * * * *